The Journal of the American Leather Chemists Association

American Leather Chemists Association

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VOLUME X, 1915

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Journal of the

American Leather Chemists Association

Vol. X JANUARY, 1915 No. 1

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The American Leather Chemists Association

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BOUND VOLUMES OF THE JOURNAL.

Bound volumes of the JOURNAL for 1914, vol. IX, will be ready for delivery about January 1, 1915. They will be bound in half morocco or cloth, uniform with previous volumes; price $6.00 per volume, delivered. Copies of all previous volumes are on hand and these may be had at the same price. Members wishing to exchange unbound numbers will please send them by mail or express to the Manager, Ridgway, Pa. The exchange price is $1.20 per volume, delivered. Missing numbers will be supplied at 25 cents each.

COUNCIL MEETING.

At a meeting of the Council of the American Leather Chemists' Association, at the Chemists' Club, New York City, on Saturday, December 12, 1914 there were present Messrs. Reed, Teas, Faust and Oberfell.

Mr. Reed, Secretary.

Mr. Oberfell was selected Chairman.

The reading of the minutes of the preceding Council meeting was waived.

Question of Articles for the JOURNAL.—It was agreed that some results might be accomplished by each member of the Council writing to a number of members, asking that they contribute articles.

Mr. Reed submitted some correspondence between W. R. Cox and President Levi. It was the sense of the meeting that the plan suggested by Mr. Cox for making the JOURNAL of more interest to the Associate membership was a good one, and the Secretary was directed to write Mr. Cox that any articles he might care to submit along the lines suggested would be gladly received.

Question of Annual Meeting. Result of Vote.—Mr. Reed announced the result of the vote on the time and place of the 1915 meeting. There were 56 votes cast on the question of holding the meeting in the spring or fall; 52 in favor of the spring; 4 in favor of the fall. On the question of holding the meeting in April, May or June, there were 52 votes cast; for May 26; for June 19; for April 7. On the question of the place of

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meeting there were 56 votes cast; New York, 13; Philadelphia, 11; Washington, 11; Atlantic City, 21.

On motion, duly seconded, it was resolved: That the 1915 meeting be held in the spring, in May, at Atlantic City, the date suggested being Thursday, Friday and Saturday, May 27 28 and 29.

Messrs. Oberfell and Drueding were appointed a committee to select headquarters and make arrangements for the meeting, the committee to report back to the Council either at its next meeting or by mail.

A Committee on Program was appointed, consisting of Messrs. Smoot, Connelly and Beye, and all the members of the Council.

In accordance with Section 6 of the By-Laws the Council selected the names of twelve persons for suggestion to the electors for nomination to the office of Ordinary Member of Council.

Method for Stating Results of Leather Analysis and Uniform Report Blanks and Table for Barkometer Reading. (See Report of W. K. Alsop.) *Question of Standardizing Barkometers and Twaddell Hydrometers to 20° C.*—After a discussion of the two forms for reporting leather analysis (see JOURNAL for November, 1914, p. 481) it was decided to suggest that the following be used:

LEATHER AS RECEIVED.

Moisture	
Oil or grease	
Insoluble ash	
Hide substance	
Combined tannins	
Uncombined tannins	
Uncombined non-tannins	
	100.00
Total ash	
Sugar calculated as glucose	

After discussing the matter of reporting extract analyses it was decided that Messrs. Reed and Faust should collaborate in the preparation of two forms, the adoption of one of which is to be decided by a mail vote of the membership.

On motion, duly seconded, it was resolved that Mr. Alsop be

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continued as Chairman of the Committee on the question of table for temperature correction of barkometer readings.

It was suggested that the Chairman of the Committee should take up with the manufacturers the question of standardizing barkometers.

Disposal of Tannery Waste.—Mr. Veitch was appointed Chairman of a Committee on the question of disposal of tannery waste, with the recommendation that in appointing his Committee he select some associate members, with particular reference to those having waste disposal plants; and that he investigate the government work being done at the DeFord's plant.

Determination and Estimation of Tanning Materials in Admixture. (Report of Small.)—Mr. Rogers was appointed Chairman of a Committee on this subject, with power to appoint the members of the Committee; with instructions to investigate and verify the matter published within the last four or five years in an endeavor to arrive at a concrete result.

Free Sulphuric Acid in Leather. (Report of Mr. Rogers.)—Mr. Rogers continued as Chairman of the Committee.

Methods Dealing with Analysis in Connection with Beam-House Procedure. (Report Dr. Rogers.)—Mr. Oberfell appointed Chairman.

Miscellaneous Methods (Report of Dr. Balderston) *with Recommendations.*—This Committee is continued, with Dr. Balderston as Chairman, with power to select his Committee, but with the recommendation that he appoint Dr. Carnell, and the suggestion that there may be other lactic acid manufacturers interested. The question of sodium sulphide is left to this Committee.

Note.—There are certain recommendations of the Chairman which are to be submitted to a mail vote.

Color Valuation of Tanning Materials (Paper by Geo. A. Kerr).—It was decided to abandon this subject for a year.

Alundum Thimble: Its Use in Extraction of Tanning Materials (Report of Seltzer); *And in Leather Extraction* (Report of Smoot).—Mr. Smoot was appointed Chairman of a Committee to determine the value of the alundum thimble in water extraction in leather analysis.

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It was the sense of the meeting that the use of the alundum thimble should be abandoned in extracting tanning materials.

Official Method of Tannin Analysis (Delaney). *Question of Rapid and Slow-Cooling Methods.*—Mr. Sprague was appointed Chairman of the Committee. It was suggested that work be done on the four materials: hemlock, myrobalans, ordinary quebracho and oak bark extract, attention being devoted simply to rapid cooling and slow cooling and not to the question of rapid or slow chroming; that the regular chroming be done on these experiments.

Oils and Fats (Oberfell). *Use of Special Separatory Funnel.*—Referred to Mr. Oberfell's Committee.

Determination of Insolubles in Strong Liquors (Alsop).—It was decided to call for individual effort in this direction.

Matter of Filter Papers.—Mr. Small was appointed Chairman of a Committee on filter papers, Mr. Faust to be put upon the Committee. It was suggested that 1-F paper in sheets be tried out; also the new alundum filter.

Question of Decimal Point in Analysis. Referred to Committee on Forms of Reports.—It was decided to leave it the way it is.

Moellons, Hard Greases and Hydrogenated Oils (Faust Proposed Method for Unsaponifiables.) (See minutes and page 29, Official Methods.)—Mr. Faust was continued as Chairman.

Mr. Faust suggested the publication of the Munson & Walker Table for glucose in the Official Methods.

Three active and four associate members were elected.

At the meeting in Chicago, Oct. 31, 1914, Messrs. Louis E. Levi, W. H. Teas and H. C. Reed were appointed members of the Tanning School Committee.

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PROFESSOR PROCTER HONORED.

Under the above title the *Leather World* of Nov. 19 notes the conferring on Henry R. Procter by Leeds University of the honorary degree of Doctor of Science. The address on this occasion was by Professor Arthur Smithells, and is in part as follows:

"Nothing has been more characteristic of our University than its effort to bring high learning into close association with the practical arts. Success depends in the end on the men who are placed at the head of our departments, and certain it is that no one could be found who exhibits more fully than Professor Procter the qualities we should desire to see in a professor of applied science.

"Profoundly learned in the sciences that underlie his art, experienced in its practical pursuit, fired by the ardor of a discoverer, and imbued with a love of all liberal studies, he has shown the way to all who would walk rightly in the difficult path. A devoted teacher and friend of his pupils, a continual help to his colleagues, and an eager participator in all affairs affecting the welfare of the University, his services have been of inestimable and most memorable value.

"The retirement of Professor Procter from the headship of his department disclosed a degree of appreciation which took a form unique, I believe, in the history of Universities. We had hoped at this time to be assembled in celebrating the inauguration of the Procter International Research Laboratory on the premises of our University, a memorial springing from a world-wide esteem for our Professor and a world-wide appreciation of his work.

"This celebration is delayed; the incidence of war has for the time blotted out the fair and hope-inspiring view of the international fraternity of learning. We have had to accept the generous offer of Professor Procter to sacrifice his well-earned leisure, and return for a time to our active service. The University, however, will not on that account delay conferring upon him such timely honors as it can bestow.

"Twenty-five years ago I was the messenger sent by the Yorkshire College to call Professor Procter to Leeds, and so to-day I am honored with the duty of presenting him for a mark of recognition given to faithful and distinguished service."

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PROPOSED UNIFORMITY IN METHODS OF FAT ANALYSIS.*

By W. Fahrion.

At the last Congress of the I. A. L. T. C. in 1912, a commission was appointed to study the above question in so far as it relates to materials used in tanning. The members of this commission, including one additional collaborator are Dr. G. Baldracco, Turin (designated in this report as Ba), H. G. Bennett, Beverley (Be), H. Brumwell, Leeds (Br), Dr. W. Fahrion, Stuttgart (F), J. L. van Gijn, Waalwijk (G), Dr. J. Paessler, Freiberg (P), J. Schneider, Prague (S), Urbain J. Thuau, Paris (Th), and J. T. Wood, Nottingham (W). The chairman, Dr. Fahrion, sent out in October, 1912, a circular outlining a plan of work. It was specified that any method of analysis in general use might be employed, provided it be clearly described.

In February, 1913, samples of the following oils were sent to the members: (1) German cod-liver oil, (2) Newfoundland cod oil, (3) whale oil, (4) herring oil, (5) Spanish sardine oil, (6) Japanese train oil (Japantran), (7) linseed oil, (8) neatsfoot oil, (9) sod oil (degras). The time limit for submitting reports was set at March 1, 1914. Unfortunately most of the members were hindered by illness, pressure of work, etc., so that only one, van Gijn, sent in a report by the time specified.

The Italian section had expressed the wish that the commission should not confine its work to the matter of analysis, but should also take up the related practical questions, such, for example, as to define between what limits the analytical constants of a given oil should lie in order that it shall be considered suitable for a specified use. This wish is intelligible and commendable, but it seems too early to attempt to define such limits.

The question naturally comes up, what agreement between collaborators may be expected in the use of recognized methods. In case the results are not sufficiently concordant, a second question arises, how to change the methods so as to promote a better agreement. It may be remarked that the second question is not merely an academic one, for the differences shown in the analytical results are notably greater than might have been expected.

* *Collegium*, 1914, p. 599. Translation for JOURNAL A. L. C. A.

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I. Acid Value.

The content of free fatty acid was with one exception reported in mg. of KOH per gram of oil. For the sake of better comparison the results in the following table are figured to per cent. of free fatty acid by means of the factor $561/282 = 1.99$.

TABLE I.—Acid Value.*

Analyst	German cod	Newfoundland cod	Whale oil	Herring oil	Sardine oil	Japanese train oil	Linseed oil	Neatsfoot oil
Ba	20.24	29.28	0.98	17.77	18.71	17.31	6.45	8.64
Br[1]	18.9	28.42	0.86	19.2	19.0	16.8	6.7	8.53
F	20.2	29.2	1.0	16.9	19.0	16.7	6.1	8.7
G	18.4	26.8	0.9	16.4	17.2	16.7	5.7	8.0
P	20.45	26.0	1.25	17.85	18.9	17.4	6.3	8.95
W[2]	16.4	—	0.60	16.71	17.73	16.1	5.35	8.56
Greatest difference...	4.05	3.3	0.65	2.8	1.8	1.3	1.35	0.95

* Translator's Note—The term here used is Säurezahl, and should be translated acid number. So the author uses Jodzahl, which is rendered iodine value, and Verseifungszahl which is translated saponification *value* instead *number*, following what seems to be the usual custom in English.

[1] Brumwell had as collaborators F. E. Thompson, W. R. Johnson, C. Muckenhirn, D. Woodroffe, F. C. Barber and E. E. Wilkinson.

[2] The work was done by D. J. Law.

The differences are very considerable. The marine oils, however, are easily altered, and I do not doubt that some of them at least, have risen in acid value during the year, so that those observers whose work was done first find the lowest values. This is especially noticeable in the case of the cod oils. In the case of the very stable neatsfoot oil the differences are smaller: leaving out the lowest value brings the variation down to 0.4. In fact, we may allow differences as high as 0.5—perhaps somewhat higher, Brumwell suggests—as due to personal equation. In view of this there seems no object in carrying acid value to 2 decimal places.

When alcohol alone is used as solvent for the free fatty acids and soaps, a weak point in the method may be noted, for some glycerides are decomposed by boiling with alcohol. It is well known that the titration may be carried out in the cold if instead of alcohol, petroleum ether or ether be used as a solvent. In the first case it is necessary to note that Holde has found that

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when an alcohol soap solution is shaken with benzene, a slight dissociation of the soap takes place as soon as the alcohol contains as much as 20 per cent. of water, and he accordingly recommends titrating with alcoholic potash. For this reason I have in the plan of work expressed the wish that a comparison of the above-mentioned methods be made. To this wish several of the collaborators responded.

Baldracco, using 5 grams of substance and N/10 alkali obtained results shown in Table II.

TABLE II.

	Alkali solution	Alcohol	Alcohol and pet. ether	Alcohol and ether
German cod-liver oil	Alcoholic	20.26	20.24	20.18
	Aqueous	20.25	20.26	20.21
Newfoundland cod oil...	Alcoholic	—	—	29.22
	Aqueous	29.27	—	29.29

This is a remarkable agreement, and Baldracco concludes that the solvent is immaterial. He prefers alcohol and petroleum ether or alcohol and ether because these permit titration in the cold and the solution remains clear. He can perceive no advantage in the use of alcoholic potash.

Brumwell has made a similar comparison with the same oils, Johnson, Muckenhirn and Thompson collaborating. He used 2 to 3 grams of substance and N/10 alkali. Results are given in Table III.

TABLE III.

	Alkaline solution	Alcohol	Alcohol and pet. ether	Alcohol and ether
German cod-liver oil	Alcoholic	18.7-19.0	18.4-19.1	18.4-19.3
	Aqueous	18.6-19.3	18.7-19.2	18.9-19.2
Newfoundland cod oil...	Alcoholic	28.0-28.5	28 5-29.2	28.7-29.1
	Aqueous	27.9-28.2	28.0-28.6	28.2-28.6

I cannot get as good agreement as Baldracco shows, obtaining for cod oil the following result, using 5 grams of substance and N/10 alkali: with alcohol alone, 28.9, with alcohol and petroleum ether 28.8 and with alcohol and ether 29.3.

Van Gijn used 3 to 5 grams of substance and N/5 alkali and obtained with alcohol and ether practically the same results as with alcohol alone, as follows: German cod-liver oil 18.4-18.45, sardine oil 17.2-17.1, linseed oil 5.7-5.7, and for neatsfoot 8.0 and 8.0.

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It would seem from the above results that no important purpose is subserved by an attempt to make comparative examinations of the acid value of marine oils, since their content of free fatty acids rises on standing. In order to establish this point, I desired the collaborators to preserve the samples and test their acid value, etc., from year to year. It is to be expected that the oils having a low iodine value will show themselves fairly stable while those with higher iodine value will change with exposure to varying conditions of temperature, light and access of air.

Considerable variation in practice is seen in the determinations of acid value which were submitted. I should recommend the use of at least 5 grams of substance, or in the case of high acid values even more, and that the alkali be N/5 or N/2. If N/10 alkali is used, and the acid value is high, the alcohol of the solution is seriously diluted by the titration. The water percentage must not pass 50 per cent., on account of the danger of dissociation of the soaps.

II. Saponification Value.

In the plan of work, the usual method was prescribed, but it was desired that the concentration of alkali and acid used should be stated as well as the time of boiling in saponification. These particulars are given in Table IV.

TABLE IV.

Observer	Weight used grams	Quantity and concentration of alkali	Time of boiling	Concentration of acid
Ba	1-2	25 cc. N/2	½ hr.	N/2 HCl
Br	2-3	N/2	½ hr.	N/2 HCl
F	3-4	40 cc. N/2	5 min.	N/2 HCl
G	about 2	N/2	2 hr.	N/5 H_2SO_4
P	1-2	25 cc. N/2	1 hr.	N/2 HCl
W	1.5-2	25 cc. N/2	½ hr.	N/2 H_2SO_4

Brumwell ran a blank, and I also usually do this, but the titration of the alkali changed hardly at all with short boiling. The other collaborators give no report on this point. Results are given in Table V.

Here the agreement is not close enough. The cause of the differences may be sought as before in the ease with which the marine oils change in composition. I carried on a research in

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TABLE V.—SAPONIFICATION VALUE.

Chemist	German cod-liver oil	Newfoundland cod oil	Whale oil	Herring oil	Sardine oil	Japanese train oil	Linseed oil	Neatsfoot oil
Ba	184.8	178.7	185.64	183.3	191.0	183.3	187.0	194.0
Br	184.7	179.5	182.5	183.6	186.7	184.3	191.6	—
F	186.0	179.5	186.3	181.6	190.9	184.5	190.0	193.8
G	186.4	178.6	188.3	187.3	193.3	185.2	190.0	197.0
P	178.6	171.3	182.0	176.4	185.7	176.6	188.1	192.7
W	182.5	—	182.8	179.9	189.2	181.2	186.1	193.4
Greatest difference	7.8	7.3	6.3	10.9	7.6	9.9	5.5	4.3

this direction years ago.[1] Oils with low iodine value, such as whale oil and Japanese oil, gave values in good agreement while oils with high iodine value (for example sardine oil), rise further in saponification value the longer the alkali works, the greater the excess of alkali and the more water the alkali contains. I can therefore conclude, on the basis of these experimental results that from the highly unsaturated fatty acids of the marine oils are formed by the splitting process, small amounts of liquid fatty acids of low molecular weight (73.9 and 76.8). The cod-liver oil examined at that time was, however, an exception, giving constant values.

In agreement with these conclusions are the results of van Gijn, who by 2 hours boiling obtains in nearly every case the highest saponification value. His figures for neatsfoot oil being omitted the others show a sufficiently close agreement. In the case of linseed oil the differences are less than in the case of the marine oils. These, however, are still too high, although variations of 2 or perhaps even 3 units may be permitted between the results of different observers. I believe that both in the case of linseed oil and of the marine oils concordant results may be obtained if the following points are carefully observed: (1) at least 3 grams of oil should be taken. (2) The alkali should contain as little water as possible, at most under 10 per cent. It is best to dissolve the caustic alkali directly in 96 per cent. alcohol, or a twice normal alcoholic solution containing 10 or 15 per cent. water may be diluted with 3 or 4 times its volume of 96 per cent. or of absolute alcohol. (3) Two hours or even ½ hour is much

[1] *Chem. Review* 1899 p. 25.

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too long to boil true oils or fats. Such directions were 10 years ago copied from one text book into another. The moment when the saponification is complete may be readily observed. The fat goes into clear transparent solution. If the solution is then boiled only a few minutes it is certain that there will be no unsaponified fat remaining. (4) In titrating back the water content of the solution must not rise above 50 per cent.

III. Iodine Value.

In the plan of work the desirability of estimating the iodine value by both the Hübl and the Wijs method was suggested. It might be thus determined whether the Wijs method always gives higher results or only in the case of the highly unsaturated oils, or finally, as some have maintained, whether if carried out with sufficient care the two methods will always give similar results. Brumwell used the Hanus method. Results are given in Table VI.

TABLE VI.—Iodine Value.

Chemist	Method	German cod-liver	Newfoundland cod	Whale oil	Herring oil	Sardine oil	Japan train	Linseed	Neatsfoot
Ba	Hübl	149.4	136.9	97.9	91.6	156.2	93.5	149.0	68.6
Ba	Wijs	167.2	150.0	118.1	114.5	193.6	109.9	172.0	77.6
Br	Hanus	158.4	145.9	114.0	116.5	168.6	107.7	165.6	75.7
F	Hübl-W	156.3	141.4	113.2	109.5	182.2	106.2	165.0	77.7
F	Wijs	165.1	149.7	117.0	114.2	190.9	110.4	173.7	77.6
G	Hübl	155.0	145.3	114.2	110.6	177.4	107.4	164.9	76.0
G	Wijs	166.0	150.3	117.8	114.6	192.3	110.4	173.8	78.0
P	Hübl	159.8	140.3	105.3	113.4	171.6	106.9	164.2	77.0
W	Hübl	148.3	—	113.9	114.3	173.5	105.7	163.9	77.6
Greatest difference	Hübl	10.4	8.4	16.3	21.8	26.0	13.9	16.0	9.1
	Wijs	2.1	0.6	1.1	0.4	2.5	0.5	1.8	0.4

While the differences among the Hübl values are alarmingly high, those of the Wijs values are pleasingly low. This speaks well for the Wijs method and shows conclusively what has already been shown, that it is advisable to abandon the Hübl method entirely and use that of Wijs only. It is a cause of a certain regret to come to such a conclusion about a method which has been in use for years and has rendered such valuable service all this time that it is hard to let it go.

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The good agreement among the Wijs results shows that the cause of the difference in the Hübl values is not to be sought in the oils themselves, since we here see the iodine value remaining constant for a year. We may select figures from the tables, for example Japanese oil 106.2, 107.4, 106.9, 105.7; linseed, 165.0, 164.9, 164.2, 163.9, as proof that the Hübl method properly carried out by various hands must yield results which vary at most by less than 3 units.

One point in the correct carrying out of the method is that the Hübl solution must not be too old, since by standing not only does it lose in strength, but becomes slower in action. Wood states that he mixes the iodine and sublimate solutions immediately before using, while Baldracco and van Gijn mix them 24 hours before use. My Hübl-Waller solution was about 8 days old. This solution is well known to be more stable than the hydrochloric-acid-free Hübl solution; according to a recent research it is even more stable than the Wijs solution. I think it is important to run a blank, in order to fix the titer at the beginning and end of the determination, as Baldracco does.

In regard to the time of the reaction, it was long ago shown that Hübl's assumption that the iodine absorption reaches a maximum in 6 or 7 hours, only holds for iodine values under 100. For highly unsaturated oils like linseed and fish oil the Hübl solution must work for 18 or even 24 hours. Baldracco's figures obtained by a reaction only 6 or 7 hours are therefore all too low. In the case of the Wijs method the time of reaction can have no such important effect, for by it van Gijn gets the same result in 4 to 6 hours that Baldracco and I do in 1.

The question of excess of iodine is very important for the Hübl method. In any determination not more than half the iodine present must be used, or in other words the excess must be at least 50 per cent. of the total iodine. If this point is not looked out for, too low values will result in the case of linseed and fish oils. The Wijs solution seems to require an excess of 50 per cent., although Wijs himself prescribed an iodine excess of 75 per cent.

Further, the table shows that Tolman and Munson[2] were right

[2] *J. Amer. Chem. Soc.*, 1903, **25**, 244; 1904, **26**, 826.

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in the statement that for values under 100, the Wijs' method agrees with Hübl's, while for iodine values over 100 it gives higher results than Hübl's. Which value in the latter case is nearer the truth is not established with certainty. In the case of the fatty acids the Wijs value is very close to the theoretical, as Meigen and Winogradoff[3] have recently found. The same is true of earlier researches and also for the Hübl value. Brumwell's results by the Hanus method with one exception agree with Hunt's[4] statement that for highly unsaturated oils the Hanus figure lies between those of Wijs and Hübl.

IV. Unsaponifiable.

In the plan of work it was judged desirable to find the upper limit of unsaponifiable content for marine oils. For the estimation of unsaponifiable the method of Hönig-Spitz was indicated. Contrary to expectation, the agreement on this determination leaves much to be desired. Results are shown in Table VII.

TABLE VII.—Unsaponifiable.

Per cent.

Chemist	German cod-liver	Newfoundland cod	Whale	Herring	Sardine	Japan	Linseed	Neatsfoot
Ba	1.09	1.59	—	—	—	—	—	—
Br	0.82	0.55	0.23	0.50	0.10	1.00	1.10	0.62
F	1.19	3.16	0.52	1.01	0.26	0.98	1.57	0.52
G	0.66	0.21	0.27	0.87	0.24	0.63	1.43	0.26
P	1.6	2.50	1.60	2.00	—	1.60	1.90	1.20
W	2.04	—	1.48	1.77	0.75	1.43	2.99	0.92
Greatest difference	1.38	2.95	1.37	1.50	0.65	0.97	1.09	0.94

The differences here are due no doubt to the methods of determination which are quite different. Baldracco mixes the soap from 20 grams of oil with sodium bicarbonate to convert the free alkali into carbonate, then with coarse sand dries the mixture at 120°-130° C., extracts it in a soxhlet with water-free ether and washes the extract twice with water. He prefers these methods to others because the results agree well, because by repeatedly saponifying the unsaponifiable so found no appreciable

[3] *Z. angew. Chem.*, 1914, **27**, 241.

[4] *J. S. C. I.*, 1902, **21**, 454.

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loss of weight takes place, and because in shaking out the soap-solutious emulsions difficult to break often form.

The last objection is not insuperable, for a suitable addition of alcohol always prevents emulsions. Against Baldracco's method I have two considerations. The unsaponifiable of marine oils doubtless contains beside cholesterin a series of other substances about which we know nothing. Among these there may be some which are vaporized or destroyed by a temperature of 120°-130° C. Wood notes that the unsaponifiable of sardine oil loses weight even at 100° C. Beside this negative source of error, a positive one is not excluded. Ether dissolves soap to some extent. The washing with water is done to remove this soap taken up by the ether. The water not only dissolves but dissociates the soap, and the fatty acid split off dissolves in the ether and remains to raise the result. Unfortunately Baldracco has done only two. His result on cod is probably too low.

Brumwell and van Gijn have worked by the Hönig-Spitz method. Their results are too low, at least for the most part, because they used too little petroleum ether and did not shake out the solution often enough. The Hönig-Spitz method dates from 1891, and its authors used it in the first instance for the estimation of mineral oils in fatty oils. For this it is eminently suitable. For the estimation of unsaponifiable in marine oils it has the disadvantage that cholesterin and phytosterin and apparently also other constituents of the unsaponifiable matter are very difficultly soluble in petroleum ether, so that a large quantity of the solvent must be used. For instance, Paessler dissolves the alkaline soap from 10 grams of oil in 100 cc. of 50 per cent. alcohol and shakes it out 3 times with 100 cc. portions of petroleum ether. The united ethereal solutions are 3 times washed with water, against which washing lies the same objection as in the case of Baldracco's process. Besides, Paessler boils for the purpose of saponification for 3 hours, which involves entirely unnecessary work.

My values were obtained by the following method: About 5 grams of oil were saponified by brief boiling with 20 cc. of twice-normal alcoholic alkali plus 10 cc. alcohol. The soap solution was diluted with 25 cc. of water and shaken out with 4

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or in some cases 5 successive 50 cc. portions of petroleum ether, the united ethereal solutions washed once 20 cc. of 50 per cent. alcohol which dissolves the soap without dissociating it.

Wood determines the unsaponifiable by a rapid method which was given him by J. M. Wilkie. Five grams of oil are boiled an hour with 12.5 cc. of twice-normal alcoholic potash under a reflux condenser. The soap solution diluted with 50 cc. of water, shaken out with 40, 30 and 20 cc. of sulphuric ether and the combined ethereal solutions washed 3 times with water. This mtehod, we in Germany call Bömer's, and I have pointed[5] out its advantages and disadvantages as compared with that of Hönig and Spitz. Its chief advantage lies in the fact that the unsaponifiable matter is far more easily soluble in ether than in petroleum ether; its disadvantage is due to the considerable solvent effect of the water-containing ether upon the soap, and this soap dissolved by the ether is as before noted dissociated by washing with water. In the case of a linseed oil I have found unsaponifiable so held which was positively acid and also entirely soluble in petroleum ether. It requires therefore to be purified, and this Bömer himself did by a second saponification. It is sufficient, however, to warm it with a little alcohol, neutralize, evaporate, and take up the completely water-free residue in petroleum ether. Since Wood has not undertaken such a purification, we may regard his results as probably high. Unfortunately I have not found time to apply Bömer's method to these 8 samples, so I cannot be sure that it would even with the purification of the unsaponifiable give results higher than the Hönig-Spitz method. The latter is the most convenient, even considering that one must shake out the solution several times and with relatively large quantities of petroleum ether.

IV. Degras Analysis.[6]

Five collaborators have analyzed the sample of sod oil, and obtained the following results:

[5] *Chem. Ztg.*, 1907, 31, 435.

[6] Compare Fahrion, *Collegium*, 1911, p. 53; Abstract this JOURNAL., 1911, p. 202.

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TABLE VIII.—Sod. Oil..

	Ba	Br	F	G	P
Water, per cent.	24.16	22.6	22.6	23.6	—
Ash, per cent.	—	0.7	0.6	0.8	—
Unsaponifiable, per cent...	1.79	0.7	1.0	1.12	1.2
Fatty acids, per cent.....	53.14	49.2	52.0	—	—
Oxy-acids, per cent.....	13.23	14.3	13.0	14.4	—
Water-sol. oxy-acids, per cent.	—	—	2.9	—	—
Acid value	52.64	—	52.8	54.7	50.6
Saponification value.....	164.69	—	—	—	159.4
Iodine value, Hübl.....	37.12	—	52.3	—	52.2
Iodine value, Wijs.....	58.48	—	—	—	—

For water estimation Baldracco mixed 5 grams of substance with the same weight of pieces of glass and heated in a water oven to constant weight. The drying took 47 hours. He recommends also another method which is a modification of the proposed method for determining the water in milk. A glass dish is weighed with a stirring rod. Into it weigh 5 grams of the degras. Add 5 cc. of acetone and heat on a water bath at 60° C. with stirring until all the acetone and most of the water have evaporated. Then heat in a water oven to constant weight. This process took 19 hours and gave 24.10 per cent. water instead of 24.16 per cent.

For such a method I believe alcohol is better suited than acetone. If 5 grams of degras are weighed into a platinum dish with stirrer, weight of dish and stirrer being known, and evaporated on the water bath with 5 cc. of alcohol, the process being repeated with stirring until no further loss of weight occurs, the water content of the degras can be found in less than 19 hours. My method (Baldracco incorrectly calls it Ruhsam's) can be carried through in 15 minutes. The water is directly boiled off in a platinum crucible. This method gives not too low results, as Baldracco claims, but, if correctly carried out, (which is not at all difficult), correct ones. Differences of ½ per cent. are naturally permissible, and if the difference between van Gijn on the one hand and Brumwell and myself on the other is greater than this, the fault does not lie in the method, but in the long standing of the sample. My sample had separated, a lower layer, lighter in color and with higher water content plainly showing. It was therefore thoroughly mixed again in a wide dish. For this pur-

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pose a gentle warming was necessary, which caused a slight evaporation of water.

In the case of oxy-acids differences of ½ per cent. or thereaway are clearly explainable, chiefly for the reason that the oxy-acids are not insoluble in aqueous hydrochloric acid, and the amount dissolved varies with the amount of water and the excess of acid. In order to estimate this dissolved portion, the hydrochloric acid solution is completely dried, the residue taken up in a little ammonia or aqueous alkali and this solution shaken out in a small separatory funnel with petroleum ether and hydrochloric acid. In all cases the ash of the oxy-acids should be noted.

I estimate the iodine value and the acid value on the water-free degras, calculating them in the cases under consideration from the water-containing material for the sake of comparison.

Of other constants whose determination was desired in the plan of work, mention may be made of the content of solid fatty acids and the hexabromide number. The former is of importance in judging of neats-foot oils and the latter in the case of linseed and fish oils. The determination of these is notably more difficult and time-consuming than is the case with the other constants. So few data have come to hand that the matter will have to be taken up again later.

EDITOR'S NOTE.—The following statement of the Hönig-Spitz method for unsaponifiable, mentioned in Dr. Fahrion's report, is from *J. S. C. I.*, 1891, p. 1039. From 7 to 10 grams of fat are saponified with alcoholic potash, if necessary under a vertical condenser; 30-40 cc. of water added, the mixture boiled up, cooled, transferred to a separatory funnel, the flask rinsed with 50 per cent. alcohol and then with 50 cc. of petroleum ether, which is added to the contents of the funnel. The petroleum ether separates rapidly from the alcoholic soap solution, and after the latter has been run off is treated with 10-15 cc. of 50 per cent. alcohol 2 or 3 times. The treatment with petroleum ether is repeated to extract the remainder of the unsaponifiable matter; usually 3 extractions suffice. With materials which are saponified with difficulty, it is advisable to repeat the saponification and subsequent operations.

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CELAVINIA AND BABLA.*

Their Properties, Reactions, Classification and Practical Value.

By Hugh Garner Bennett, M.Sc., F.C.S.

When a new tanning material is introduced to the trade there is always a certain amount of suspicion attached to it. It is certainly a very important matter to consider what kind of leather it is likely to make, and how it is likely to modify a tannage when used in a blend along with the better-known tanning materials. It is very useful to be able to classify it as belonging, on the whole, to one definite class of tanning materials. Even if the classification is a trifle rough-and-ready, it is of practical importance to know whether any new material produces effects like valonia, or myrobalans or quebracho.

It is proposed in this article to indicate some of the reactions and properties of two of the newer tanning materials, namely, celavinia and babla, with a view to discover their relation to the older and better known tanning materials. In this way the tanner will be able to judge how best they may be employed for any specific practical purpose, and which of the commoner materials they may be able to replace in the tanyard.

Celavinia.

The pods named "celavinia," "celavina," or "cevalina" are supposed to be derived from "caesalpinia tinctoria," which grows in Central America and the Western parts of South America. These pods have been before the trade now for some time as a tanning material capable of producing a particularly light-colored leather. So far as this particular claim is concerned, celavinia certainly comes up to its reputation. The writer has tanned some pelts with celavinia only, and obtained a satisfactory leather which is almost white in color. Celavinia certainly produces a lighter colored leather than any other natural tanning material with which the writer is acquainted. This is the practical result which follows from the fact that celavinia contains no coloring matter associated with its tannin. Many other tanning materials have associated with the tannin they contain a characteristic coloring matter, *e. g.*, sumac contains myricetin, which is only one

* *Leather Trades Review*, Nov. 18, 1914.

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of a group of similar compounds (quercetin, fisetin, etc.) grouped together under the general name of flavones. Therefore one characteristic of celavinia is that it contains no flavone.

In fixing the nature of any tanning material, and assigning it to any place in the general classification, one of the first and most important matters to decide is whether the material falls into the group of catechol tannins, or the group of pyrogallol tannins. These groups are fairly definite, and the properties and reactions of the typical members of each are very sharply marked by their different behavior towards a series of reagents commonly employed for this purpose. It is, therefore, not a very difficult matter to decide whether a tanning material belongs to one group or the other. Taking two of the most important of these reactions, a pyrogallol tannin may be recognized when its aqueous infusion gives no precipitate with bromine water, and gives a blue-black color with a 1 per cent. iron alum solution. Now celavinia behaves in this way, and may therefore be defined as a pyrogallol tannin.

The other reactions of pyrogallol tannins confirm this conclusion. The most important of these may be mentioned:

1. Celavinia infusion gives a precipitate with copper sulphate and ammonia, insoluble in excess of the latter. This precipitate is dark colored.

2. Celavinia infusion develops a green color when allowed to stand with the addition of a sodium arsenate solution. This test (given by all pyrogallol tans) indicates the presence of free gallic acid in the infusion.

3. Celavinia infusion gives a negative result with the stannous chloride reaction, with the deal shaving reaction, and with the sulphuric acid test.

All these results are in harmony with the behavior of an ordinary pyrogallol tannin, therefore, celavinia has very little in common with quebracho, gambier, cutch, hemlock, oakbark, mimosa bark, mangrove, larch-bark, and other catechol tannins. Evidently it is closely connected with that group of tanning materials of which sumac, myrobalans, valonia, oakwood extract, chestnut extract, and algarobilla are typical members. The sub-classification of this last group of materials has been made

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possible recently by some new tests discovered by the writer, and published elsewhere. According to this suggestion, valonia, oak-wood and chestnut may be easily distinguished from sumac, myrobalans and algarobilla by the iodine test. Now celavinia infusion gives a purple red color with the iodine test, and consequently it is more nearly related to the sumac than to the valonia group. This is confirmed by its behavior towards other tests which distinguish these two sections of the pyrogallol tannins.

(a) Celavinia gives a blood red color with the chromate test.

(b) It gives no color with an aqueous solution of potassium ferricyanide.

(c) It gives an orange color with an ammoniacal solution of ferricyanide.

(d) It gives an orange color with the ammonium cobaltate test.

The next question is how celavinia may be distinguished from the other members of the sumac group. This may be done with the sodium sulphite reaction. This reaction shows a red color with the valonia group, and a yellow color with the sumac group, the latter color being probably due to the flavones associated. Now celavinia contains no flavone, hence it is not surprising to find that sodium sulphite simply gives no reaction at all with celavinia.

Another point of difference is the color of the precipitate obtained with lime water. The valonia group give a yellow precipitate which turns purple; the sumac group also give a yellow precipitate which turns green. Celavinia differs from both these groups, as it gives with lime water a white precipitate, turning blue. The difference from the sumac group may again be explained by the absence of any yellow coloring matter in celavinia. If celavinia contained myricetin, it would doubtless act like sumac, and give a yellow precipitate instead of white, which would have turned green instead of blue. In all respects yet considered, therefore, celavinia behaves just as sumac or myrobalans would if they were minus their flavones.

There is, however, one other important reaction not yet mentioned, namely, the nitrous acid reaction, which is common to all pyrogallol tannins, and to some catechol tannins. This reaction

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(for the details of which the text books should be consulted) indicates the presence of ellagitannic acid, *i. e.*, of that tannin which yields "bloom" (ellagic acid). Now, it is a very striking fact that celavinia does not give this reaction. Celavinia does not contain ellagitannic acid, and yields no bloom. In this respect it is alone among all the other pyrogallol tannins. In this connection it is noteworthy that gallotannic acid, the purified tannin of galls, also gives every reaction common to the sumac group, but does not give the nitrous acid reaction. Gallotannic acid also gives no color with sodium sulphite, and with lime water gives a white precipitate, turning blue. In short, a solution of the celavinia tannin behaves towards every known test in an absolutely identical manner to that of gallotannic acid, and it is difficult to resist the conclusion that celavinitannic acid and gallotannic acid are one and the same.

Whether celavinia tannin may not be in the future distinguished from gallotannic acid by some yet undiscovered test, it is, of course, impossible to say, but, in the meantime, their close resemblance and their sharp difference from other pyrogallol tannins in reference to the nitrous acid reaction is, in the writer's opinion, sufficient to justify the creation of a new section of pyrogallol tannins, which are typified by the reactions of these two materials.

One other point remains with regard to celavinia. With a material evidently closely related to sumac, and of excellent color, it is natural that it should be regarded as a substitute for sumac in improving the color of tanned leather. This arises from the fallacy that a material which makes a light-colored leather will make leather light-colored. It is not so. Sumac bleaches leather not because it makes a light-colored leather itself, but because it contains a reducing agent which is capable of bleaching tanned leather in much the same way as sulphurous acid. Experiment shows that celavinia contains no such reducing agent, and will not therefore bleach leather.

To summarize, celavinia may be considered to resemble sumac more than any other tanning material, but it differs from sumac in three very important respects, *viz.*:

1. It contains no coloring matter or flavone (myricetin).

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2. It contains no ellagitannic acid. (Sumac certainly contains very little.)

3. It contains no reducing agent capable of bleaching leather.

All things considered, there should be an opening for this material in tanning light leathers where color is important, and in manufacturing light-colored extracts. It may be of interest to add a typical analysis.

ANALYSIS OF CELAVINIA BY I. A. L. T. C. METHOD.

	Per cent.
Tannin	= 31.9
Soluble non-tannins	= 19.2
Insoluble	= 43.1
Water	= 5.8
	100.0

Tintometer:

Yellow	= 0.8
Red	= 1.6

BABLA.

This name, sometimes applied to the pods of *Acacia arabica* (babul, Egypt; sant or sunt, Sudan; gabarrua, Nigeria), is also applied to the pods of *Acacia Cineraria, Acacia vera,* and other species. Which species corresponds to the material now on the market as "babla" is somewhat doubtful, for the tannin of babla is certainly different from the description of *A. arabica* by Procter, who says that the latter gives no precipitate with bromine water or lime water. An infusion of babla gives a blue-black color with iron alum, so that babla tannin cannot be a typical catechol tannin. It also gives a decided precipitate with bromine water, so that it cannot be regarded as belonging to the ordinary pyrogallol tannins. Materials behaving in this way have been classified by Procter under the heading of "Mixed or doubtful," but it seems nearer the mark to call them simply "mixed," for the behavior of the whole of the materials in this class could be summarized in the statement that they are catechol tannins either containing a pyrogallol group, or associated with compounds which contain such a group. If this view be taken, it is not surprising to find that this class of materials, of which babla is in every way typical, resemble very closely in many respects the sumac

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group of pyrogallol tans. Babla, for example, behaves exactly like sumac in the following tests:—Aqueous ferricyanide, ammoniacal ferricyanide iodine test, chromate test, cobalt test, copper sulphate and ammonia, stannous chloride, formaldehyde, lead acetate and acetic acid, etc.

On the other hand there is no doubt of its close relation to the catechol tans, for, in addition to the bromine water test, it gives the sulphuric acid reaction, and gives no reaction with nitrous acid. There is no doubt, therefore, that babla is a typical mixed tannin, partaking partly of the nature of a catechol tan, and partly that of a pyrogallol tan. It is, therefore, most closely related to the tannins of lentisco, oak bark and mimosa bark. It may be distinguished from these by various reactions, but most strikingly by the fact that babla gives the deal-shaving reaction for phloroglucol. Procter mentions a South American bark which is a mixed tannin and yet gives this phloroglucol test, but this bark seems to have little practical importance, so that babla may be readily distinguished from all the other mixed tannins by this reaction. The fact is important in another respect, namely, that one tanning material should answer the tests for catechol, pyrogallol and phloroglucol. With the exception of the "white bark" mentioned above, the writer has not met another case of this kind. Babla is indeed a mixed tannin!

It will be better just to mention the behavior of babla towards some other tests. It can then be compared to the behavior of other mixed tannins towards these reagents by reference to the text books.

(i) Babla infusion gives a green color with the sodium arsenate test.

(ii) Its phenolic compounds are incompletely precipitated by lead acetate, and the filtrate therefore gives a yellow color with caustic soda.

(iii) It gives a blue-colored precipitate with lime-water.

(iv) It develops a red color with sodium sulphite.

(v.) Its solution gives an intensely red color with a 10 per cent. solution of potassium cyanide. All tanning materials answer this test more or less, but with babla the color is much more intense than with any other material, so that this test may be

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almost regarded as typical of babla. This would seem to indicate that a babla solution contains an unusually large proportion of free gallic acid.

The following is a typical analysis of babla:

ANALYSIS OF BABLA BY I. A. L. T. C. METHOD.

	Per cent.
Tannin	= 29.6
Soluble non-tannins	= 17.2
Insoluble	= 44.6
Water	= 8.6
	100.0

Tintometer:

Red	= 1.4
Yellow	= 2.6

It will be noticed that the color is good, and the tannage of pelt with babla alone bears this out, a light-colored leather being obtained. The quality of the leather very strongly resembles that produced by gambier alone, being mellow, soft, plump, and pliable, but is rather spongy. Mellowness, indeed, seems to be characteristic of the babla tannin. An extract of babla would, in the writer's opinion, produce practical effects more like gambier than any other tanning material. The suggestion is offered to the extract manufacturer for what it is worth. It is a little difficult to assign any reason for this mellowness. It is not because it contains an unusually large proportion of non-tannins, or of mineral salts, so that one must conclude that it is simply the nature of babla tannin.

Its exceedingly "mixed" nature should ensure this material being a good tanning material. It is a blend in itself—a kind of "internal blend." Modern mixed tannages consist in a judicious blend of the different tanning materials. In babla the blend is already accomplished.

To summarize, babla is indeed a mixed tannin, so mixed that it almost contradicts itself. In its chemical behavior it resembles lentisco more than any other material, but in its practical behavior it approximates most closely to gambier. In this last connection, it is worthy of note that babla and gambier are the only tanning materials which give the deal-shaving reaction strongly

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It is conceivable that a phloroglucol tannin implies mellowness, but this is admittedly the only evidence yet.

In conclusion of this article the writer would like to mention one serious disadvantage which these two materials have in common. This is the leaching of the tannin on a practical scale.

In the case of celavinia the greater part of the tannin (like many pod tans) is not very difficult to remove, but the last portions of the tannin are not so easily leached, and yet this is necessary if the material is to possess any economic value. Moreover, when the greater part of celavinia tannin has been dissolved out what is left of the pod becomes very soft, and sometimes, indeed, softens to an almost impervious mud. This makes it unsuitable for the ordinary press leach.

In the case of babla the difficulty is rather serious. This material cannot be thoroughly leached without cracking, but the pods are so small that the average tanyard arrangements for myrobalans, valonia, etc., have no effect. On the other hand, finely ground babla would be an intolerable nuisance in the average press leach. If these two materials have found any enthusiasts, perhaps they will enlighten the readers of the *Leather Trades' Review* as to the best way of extracting them on a practical scale. Perhaps the extract manufacturer will solve the difficulty.

AVAILABLE TANNIN IN VARIOUS TANNING MATERIALS.*

*John H. Yocum and Thos. A. Faust.**

This is an effort to put practically before the tanners the ultimate efficiency of the tanning materials which they use and buy, either in the raw state or in the semi-raw state, namely crude materials or extracts.

These materials have certain values for the purpose of the tanner. In the present case these values are determined by their tanning efficiency, with no regard to their tanning character, and it has been found that the measure of the tanning efficiency is the

* Read at the Eleventh Annual Meeting A. L. C. A., Chicago, October, 1914.

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amount of tannin found in the liquors extracted therefrom, rather than that found in the raw materials.

Certain relative values are determinable from these raw materials in the liquors, which is the basis of this article, considering that tannin in liquor should be fully utilized. The amount of tannin obtained in the liquor, suitable for the tannage of the product desired by the tanner, is therefore the measure of the value of any particular tanning material to the tanner.

It follows that this relationship from several materials will vary, but that if the soluble tanning material in the liquor is determined as a new liquor and also after a reasonable length of time in the vats, some valuation or comparison between various tanning materials can be arrived at.

In this article no presumption is made that these experiments are nearer practicé than laboratory work can approximate, but we believe we have approximated tannery practice as near as possible.

It is a well-known fact that a producer of sole leather, using bark alone, can at the utmost obtain but a yield of 300 pounds of leather to 2,000 pounds of bark. This leather being of good gain, wiil be made up of from 40 per cent. to 45 per cent. of tannin, combined and uncombined. This means that a tannery using bark alone will obtain from 120 pounds to 135 pounds of tannin in the leather, or from 6 per cent. to 6.75 per cent. of the weight of the bark. These figures have been corroborated frequently by measuring and analyzing the liquors obtained from the leach houses of various tanneries. It appears that this is the average practice in using bark alone in the manufacture of sole leather.

Most barks, either hemlock or oak, will analyze from 10 per cent. to 12 per cent. of tannin, say on the average 11 per cent., and most leach houses will not show more than 2 per cent. of tannin on the average left in the spent bark, based on the weights of the new bark, leaving a margin of presumable extraction of 9 per cent. or 180 pounds of tannin per ton.

The wrong assumption is that this goes into the liquors, and that the losses in the tannery account for the difference between the actual consumption or 130 pounds, and the theoretical yield

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or 180 pounds, namely 50 pounds, or better than 25 per cent. of the tannin.

The cause of this discrepancy in the tannin of the new bark, spent bark and liquor produced, is problematical, but it is a fact that these losses are known to occur to the practical tanner; why, has never been fully explained. The losses from the liquor itself have been fairly well explained, comprising the amount of precipitated loss, runaway tail handlers, leakage, bleach, etc., but these larger leach house losses have never been measured for the different tanning materials.

In this article we hope to point to the fact that precipitation, both of tannin and non-tannins, has a tremendous influence upon the ultimate result, as it would appear from some of these data; and that the precipitation in the vats is made up largely, in many instances, of precipitated non-tannins, which would answer to the actual facts that barkometer strength decreases in the last layer, whereas purity increases. In other words, the last layer when sapped is frequently a much purer liquor than it was new, which could only be brought about by precipitation of non-tannins or their destruction by fermentation.

On the other hand, these data indicate that tremendous losses of tannin, presumably by precipitation, occur in the leach house, and that the yields, even from extracts, are not so great as would be expected, considering that these extracts had passed through the leaching operation and had already been subjected to such losses as might be occasioned by oxidation, etc. Apparently there is some other factor which is as yet unknown, and the subject needs further investigation.

For the purpose of estimating the loss in the leach house, the five following materials were selected: oak bark, hemlock bark, valonia cups, myrobalans and mangrove bark.

One hundred grams of the air dry ground sample, analysis of which had been made previously, were extracted to 1,000 cc. at 160° F. in about 2½ to 3 hours. This first liquor was analyzed, the spent tan was carefully removed from the extractor, dried and weighed. One-half of it was analyzed to determine the amount of tannin left in the first spent tan.

The remaining half of this spent tan was put in a flask, about

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700 cc. of water added, brought to a boil in 1 hour, and the solution kept at gentle ebullition for another hour. This liquor was then analyzed and called the second liquor.

The remaining spent tan was removed from the flask, dried, weighed and analyzed, and reported as the second spent tan. By this method, complete data were obtainable, so as to account for every gram of tannin all through the procedure.

It is believed that the first procedure gives the equivalent results of the first half of the leaching process, while the latter gives results equivalent to the second half. The results have all been figured to air dry materials. Owing to the fact that only portions of the original quantity were used in the second extraction, the true and only comparison is on the actual grams of tannin as figured to the original weights.

Oak Bark.

It is unfortunate that a better specimen of oak bark was not used. The results show that 67.9 per cent. of the original tannin as determined by analysis of the raw material, is removed during the first treatment or early leaching, and only 3.2 per cent. during the second or latter leaching, and that 19.7 per cent. is lost in the spent tan, leaving an unexplained loss of 9.2 per cent. Presumably, this is a precipitated loss in the leach house, but together with the spent tan, represents 28.9 per cent. of the total, 71.1 per cent. actually going into the liquors. This new bark contained 8.84 per cent. of tannin in the original air dry sample, so that the yield in the liquor was 6.28 per cent. or 126 pounds of tannin.

Hemlock Bark.

Seventy and nine-tenths per cent. was removed by first leaching, and 3.0 per cent. by second leaching; 17.99 per cent. was left in the spent tan and 8.2 per cent. was lost, showing a yield in the liquor of 73.9 per cent. Since this bark had 10.49 per cent. tannin in the original air dry sample, the yield per ton (7.76 per cent.) in the liquor was 155 pounds.

Valonia Cups.

Thirty-eight and eight-tenths per cent. tannin was removed by the first leaching, and 30.8 per cent. by the second leaching; 16.8

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per cent. tannin was left in the spent tan, and 13.6 per cent. was lost, showing a yield in the liquor of 69.6 per cent., or about the same as in the case of oak and hemlock bark. Since the cups had 30.46 per cent. tannin in the original air dry condition, the yield per ton in the liquor was 422 pounds.

Myrobalans.

Seventy-five and three-tenths per cent. tannin was removed by the first leaching, and 7.4 per cent. by the second leaching; 5.8 per cent. tannin was left in the spent tan, and 11.5 per cent. was lost, showing a yield in the liquor of 82.7 per cent. The bean had 36.14 per cent. tannin in the original air dry condition, so that the yield per ton in the liquor was 602 pounds.

Mangrove Bark.

Fifty-six and nine-tenths per cent. tannin was removed by the first leaching, and 28.4 per cent. by the second leaching; 5.3 per cent. tannin was left in the spent bark and 9.4 per cent. was lost, showing a yield in the liquor of 85.3 per cent. The bark had 40.58 per cent. tannin in the original air dry condition, so that the yield per ton in the liquor was 693 pounds.

It will be noted that oak bark, hemlock bark and myrobalans give up most of their tannin in the early stages of leaching; mangrove not so readily, while valonia has only about 3/5 of its available tannin removed in the earlier stages of leaching. The leach house loss runs from about 9 per cent., on oak and hemlock bark, to 13.6 per cent. on valonia, virtually the same as spent tan losses in practice. However, the precipitation loss in the leach house, where more drastic methods of leaching are pursued, must be much greater than here given; longer time, higher temperatures and greater exposure to the air facilitating the precipitation, and it is probable that where leaching is carried down to 1 per cent. in the spent tan, but little of the 1 per cent. removed ever gets into the liquors as available tannin. Again, a loss in the leach house occurs where hard waters are used, in addition to the loss here outlined.

Five pounds of tannin per ton of bark is the general estimate of the runaway tail handlers, so that it is evident that in oak bark, hemlock bark and valonia, not more than 65 per cent. of the

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tannin in the raw material, becomes available for use; in myrobalans and mangrove bark about 80 per cent.

In all cases the analysis of the liquors resulting from this experimental work, was immediately made and, under the conditions of extraction little opportunity for oxidation existed; the effort being to obtain liquors like practice sends from the leach house to the coolers, or similar to liquors obtained by mixing extract with liquor or water, as they would come from the mixing tank, taking no account of settlement which may occur subsequently.

The data obtained from 20° and 40° liquors indicate a very large precipitate between the coolers and the tan vats, and because it was quite impossible to obtain 40° barkometer strength liquors during our experiments for oak and hemlock bark liquors, we got such liquors from tanneries using only oak and hemlock bark, but found that they had already been subjected to cooler losses, and consequently the data thereon are of little value.

To follow this subject more as to semi-raw materials, the following work was done:

Solutions of 40° barkometer were prepared from the 9 following materials: oak bark, hemlock bark, ordinary solid quebracho extract, treated solid quebracho extract, liquid chestnut extract, sulphite-cellulose extract, valonia cups, myrobalans and mangrove bark. The solutions of the extracts were prepared by dissolving the extracts in sufficient hot water to make a 40 deg. liquor. The solutions of oak and hemlock bark were obtained from tanneries where these two materials were leached alone; the solutions of valonia, myrobalans and mangrove bark were leached in the laboratory under conditions similar to those pursued in the tannery.

The above liquors were all diluted and analyzed by the official method for liquor analysis. These diluted solutions showed a very low amount of insolubles, but on being calculated to the original liquor, which necessitated multiplying these insolubles by about 14, this being the dilution used, the insolubles showed very high.

The determinations of the insolubles in the liquors at 20° and at 40° barkometer were made by taking the solutions of the above

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strengths and filtering them through double plaited Prat-Dumas paper, allowing them to run through about 1¼ hours and then starting to collect without removing the solutions from the funnels.

Twenty cc. of solution was evaporated in the case of the liquor at 20° barkometer, and 10 cc. in the case of the liquor at 40° barkometer. In Table I, you will note that the insolubles in these liquors at 20° barkometer are considerably lower in all cases than those found by the official method; at 40° barkometer the insolubles were about the same as those found by the official method, although valonia showed a little higher, and ordinary quebracho much higher, while sulphite-cellulose showed considerably lower. We think the latter is due to the action of the sulphite on the filter paper.

These results were very surprising and contrary to general opinion, and consequently we duplicated the work throughout, using for the duplications S. & S. 590, 15 cm. filter paper. The results agreed very closely with the original results.

We also carried on some experiments dissolving the liquors in hot water in making up the official dilution solutions, but found the insolubles to be about the same. We therefore conclude that the experimental work is correct, and that the insolubles as reported by the official methods on all these liquors, are very close to the actual amount of insolubles in these liquors in the various strengths that they are used in the tannery, ordinary quebracho being the only exception.

The 40° barkometer solutions were allowed to stand for 2 weeks, and very heavy deposits of sediment were noted in the bottom of all the flasks. The insolubles at 40° barkometer strength were again determined in these liquors at the end of this time, and it was found that the insolubles in all the extracts had increased from 50 per cent. to 100 per cent. over the quantity found in the solutions immediately after preparation, excepting sulphite-cellulose which showed the same. It was also noted that the insolubles in all the raw tanning materials increased from 200 per cent. to 300 per cent.

The filtered solutions remaining on the determination of insolubles in the 40 deg. liquors at this time, were diluted according

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to the official methods, and the non-tannins determined. On comparing the non-tannins found here, with the non-tannins as determined in the solutions immediately after preparation, you will note that all of them, with the exception of sulphite-cellulose, are lower, valonia cups very much so, and myrobalans very little.

On looking at Tables I and II you will note that the increase in insolubles about equals the decrease in non-tannins in oak bark, hemlock bark, treated quebracho and chestnut, so that the tannin as shown in Table II, remains the same in the 40 deg. liquor which has stood for several weeks, as it was in the original liquor analyzed officially. In the case of valonia, the decrease in the non-tannins is the greatest, and the increase in the insolubles is almost as much, so that the tannin really shows a little higher. The same applies to mangrove bark, although the decrease in non-tannins and the consequent increase in insolubles, is very low here. Sulphite-cellulose does not seem to be affected in any way; the non-tannins remaining the same and the insolubles remaining the same in both the new liquors and in the old liquors analyzed at concentrated strength. Myrobalans, however, show a very large increase in insolubles, while the non-tannins are practically the same. This is no doubt due to the conversion of tannin into insolubles, as the fermentation in myrobalans is known to affect the tannin itself. Ordinary quebracho shows a slight decrease in non-tannins and a very large increase in insolubles, and consequently here also some of the tannin is lost by conversion into insolubles in the strong liquors. In view of the nature of this tanning material, this is to be expected.

In conducting this work, definite quantities of the extracts, analyses of which were known, were dissolved, making a 40 deg. liquor; the volume of this liquor was determined, and an analysis made by the official method, so that the tannin yield in the liquor at official dilution could be calculated. Treated quebracho shows a yield of 96.8 per cent., chestnut 93 per cent., sulphite-cellulose 92.3 per cent., and ordinary quebracho 86.1 per cent. We then calculated the percentage tannin yield in the liquors at 40° barkometer, and as noted above, all these extracts, with the exception of ordinary quebracho, showed about the same tannin yield, and consequently these extracts show the same percentage tannin yield

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in a 40 deg. liquor as they do in the official dilution. Ordinary quebracho, however, on account of the loss in tannin by precipitation, shows only a yield of about 70 per cent. after the liquor had stood for 2 weeks. Myrobalans, showing a yield of about 80 per cent. in the new liquor, showed a further loss of about 12 per cent. in a 40 deg. liquor after standing 2 weeks, so that the actual yield for tanning purposes is about 70 per cent.

TABLE I.

	Insol. in. liquor diluted officially on basis of diluted liquor	Insol. in liquor diluted officially calculated to original liquor	Insol. at 20° Bk.	Insol. at 40° Bk.	Insol. at 40° Bk. duplicate after solutions stood two weeks
Oak bark	0.02	0.30	0.13	0.27	0.51
Hemlock bark.....	0.27	0.36	0.24	0.34	0.56
Ordinary quebracho	0.096	1.33	1.01	2.06	3.10
Treated quebracho	0.021	0.28	0.20	0.22	0.49
Chestnut	0.03	0.41	0.19	0.36	0.60
Sulphite-cellulose...	0.023	0.32	0.01	0.06	0.08
Valonia	0.02	0.27	0.14	0.45	1.21
Myrobalans	0.026	0.35	0.11	0.47	1.10
Mangrove	0.014	0.24	0.09	0.20	0.48

TABLE II.

	Official non-tannins	Non-tannins 40° Bk. diluted after filtering and standing	Tannin official	Tannin 40° Bk.
Oak bark	4.84	4.62	4.99	5.00
Hemlock bark	5.49	5.17	3.89	3.95
Ordinary quebracho.....	1.09	0.80	8.11	6.63
Treated quebracho.....	1.34	1.16	8.58	8.50
Chestnut	2.65	2.31	5.81	5.96
Sulphite-cellulose	3.70	3.78	4.91	5.07
Valonia	2.90	1.72	4.20	4.44
Myrobalans	3.44	3.30	5.32	4.71
Mangrove	2.01	1.64	6.13	6.26

OAK BARK.

	Original analysis	First liquor	First spent	Second liquor	Second spent
Barkometer at 60° F....	—	6½°	—	½°	—
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Total solids	19.40	1.33	—	0.12	—
Soluble solids	16.93	1.22	5.90	0.10	5.55
Insoluble material	2.47	0.11	—	0.02	—
Non-tannin	8.09	0.62	3.17	0.08	3.23
Soluble tannin	8.84	0.60	2.73	0.02	2.32
No. grams tannin.....	8.84	6.00	2.18	0.28	1.74
Per cent. tannin.....	—	67.9	24.7	3.2	19.7

Per cent. tannin accounted for..... 90.8
Per cent. tannin lost..... 9.2
Per cent. tannin in both liquors (yield)..... 71.1

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TABLE II.—(*Continued.*)

HEMLOCK BARK (90 Grams of Bark Used).

	Original analysis	First liquor	First spent	Second liquor	Second spent
Barkometer at 60° F.....	—	6½°	—	½°	—
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Total solids	19.19	1.25	—	0.14	—
Soluble solids	17.59	1.13	7.40	0.11	6.44
Insoluble material	1.60	0.12	—	0.03	—
Non-tannin	7.10	0.46	4.69	0.09	3.91
Soluble tannin	10.49	0.67	2.71	0.02	2.53
No. grams tannin.....	9.44	6.70	1.89	0.28	1.69
Per cent. tannin.....	—	70.9	20.0	3.0	17.9

Per cent. tannin accounted for..... 91.8
Per cent. tannin lost..... 8.2
Per cent. tannin in both liquors (yield)..... 73.9

VALONIA CUPS.

	Original analysis	First liquor	First spent	Second liquor	Second spent
Barkometer at 60° F.....	—	10°	—	6½°	—
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Total solids	46.28	2.01	—	1.31	—
Soluble solids	45.07	1.96	35.61	1.26	20.90
Insoluble material	1.21	0.05	—	0.05	—
Non-tannin	14.61	0.78	16.52	0.59	9.76
Soluble tannin	30.46	1.18	19.09	0.67	11.14
No. grams tannin.....	30.46	11.80	13.36	9.38	5.12
Per cent. tannin.....	—	38.8	43.9	30.8	16.8

Per cent. tannin accounted for..... 86.4
Per cent. tannin lost..... 13.6
Per cent. tannin in both liquors (yield)..... 69.6

MYROBALANS.

	Original analysis	First liquor	First spent	Second liquor	Second spent
Barkometer at 60° F.....	—	20°	—	2°	—
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Total solids	53.23	4.35	—	0.41	—
Soluble solids	52.16	4.09	13.38	0.37	10.60
Insoluble material	1.07	0.26	—	0.04	—
Non-tannin	16.02	1.37	5.31	0.18	4.98
Soluble tannin	36.14	2.72	8.07	0.19	5.62
No. grams tannin.....	36.14	27.20	3.87	2.66	2.07
Per cent. tannin.....	—	75.3	10.7	7.4	5.8

Per cent. tannin accounted for..... 88.5
Per cent. tannin lost..... 11.5
Per cent. tannin in both liquors (yield)..... 82.7

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TABLE II.—(*Continued.*)

MANGROVE BARK.

	Original analysis	First liquor	First spent	Second liquor	Second spent
Barkometer at 60° F.....	—	14½°	—	5°	—
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Total solids	52.77	3.32	—	1.04	—
Soluble solids	51.65	3.18	32.67	1.00	6.69
Insoluble material	1.12	0.14	—	0.04	—
Non-tannin	11.07	0.87	9.13	0.28	2.65
Soluble tannin	40.58	2.31	23.54	0.72	4.04
No. grams tannin.....	40.58	23.10	12.71	11.52	2.18
Per cent. tannin.....	—	56.9	31.3	28.4	5.3

Per cent. tannin accounted for..... 90.6
Per cent. tannin lost..... 9.4
Per cent. tannin in both liquors (yield)..... 85.3

During the course of reading his paper, Mr. Yocum said, referring to the statement in a previous paper that the yield of tannin is as great when leached with hard water as when leached with pure water (see p. 489, JOURNAL for November, 1914).

The losses are rather subject to another factor, and that is the amount of acid that may be carried over or originating in the leach house to neutralize the lime. If the lime of the water is in excess of the acid that may exist, and I speak of acids stronger than tannic acid, losses will occur. If the bases are not there to an extent to completely neutralize the acids, then losses do not occur, so that this factor must be considered in all the statements.

And I would say in connection with this, my teaching is that industrial waters are to be reckoned in parts per 100,000, and potable waters in parts per 1,000,000, and if one will consider that there are, in the hardest water mentioned, 12½ parts to the 100,000, and looking at it as compared with other waters, some of which I have had run as high as 400 parts to the 100,000, 12½ parts is a rather soft water.

There is another factor that comes in that is the wastage in the tail handlers. I am speaking of sole leather. The ordinary habit is to waste sufficient liquor to keep the yards clean. This is estimated, and I admit that it is an estimate, but I have based it on 500 hides in a 50,000 pound vat, where the wastage was ½ of the vat per day, and that the maximum tannin in the liquor

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would not be over ½ of 1 per cent. Under such conditions 5 pounds of tannin per ton of bark is wasted in the runaway.

At the conclusion of his paper, Mr. Yocum made the following remarks:

As a summary of this I would call your attention to the fact that the analytical results given you on a raw material do not by any means indicate what you are going to get in your liquors for tanning purposes. It would appear, to me, and practice rather bears me out, that the analysis of a raw material under the conditions of extraction indicate more than is really the result. You would get in the neighborhood of from 60 to 65 per cent. on oak and hemlock bark and valonia, and about 75 per cent. on myrobalan, with about 80 per cent. on mangrove, and in the purchase of extracts you would range from the highest, that is sulphited or treated quebracho of 96 per cent. down to the lowest, untreated quebracho of about 70 per cent. So that while the chemist cannot do other than report what he finds, it is necessary for the tanner to estimate from that how much he is really going to get into his liquors for tanning purposes.

These estimates are, I will admit, somewhat crude, and possibly should be followed up more carefully, but I am sure of my premises, that you are not getting into your liquor the amount of tannin you are purchasing. Now there are other factors that go with that: The inefficiency of your tannery. But also let us understand that there is a weakness in the analysis and the mixing of these extracts. The chemist gives you the maximum, and if you can't get it it is your fault. But there are some factors now that will not permit you to get the total of what the chemist gives you.

Mr. Balderston said that in the case of valonia, with the experimental leach house method the amount of tannin obtained in the liquor was as much as the analysis showed, and when there is added what was found in the spent material the total is a good many more pounds per ton than the analysis showed. The same is true of quebracho wood; there was actually more tannin in the liquors than the analysis showed. In the case of hemlock bark, there was a small loss.

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Mr. Yocum asked why we cannot make 500 pounds of leather from a cord of bark instead of 300.

MR. BALDERSTON: I don't know. But I do know this, that the trouble of which you speak, and which is, of course, something that every tanner wants to know all about, occurs chiefly somewhere else than in the leach house, if the leaching is managed well.

MR. KELLY: Mr. Chairman, I would like to ask whether I interpreted his figures in regard to the pounds of tannin per cord of bark in the liquors used in the tanning of hides, in making of leather, correctly? I believe he stated that of 180 pounds, according to the analysis of the fresh material, which should be in the spent tan, and in the liquors only, 130 pounds was accounted for. Am I correct in that or not?

MR. YOCUM: Well, accounted for in the *leather*.

MR. KELLY: I understood that he was talking at the time about the liquor, making a difference there of about 50 pounds of tannin per ton of bark. I would just say that in my experience in taking samples of fresh bark on a week's run in the tannery under practical working, not in experimental ways in the laboratory, and of analyzing the liquors and figuring back from the quantities and strengths of the liquors, on a week's run, corroborated on three different occasions of about a month apart, that I got within about ¼ of 1 per cent. of the tannin that the analysis of the material shows. Now the reason I mentioned that is because I believe that Mr. Yocum said that that other 1 per cent. that might be removed by drastic means was not gained in the tannery, or was not in the liquor in an available form. But it was in these liquors, after standing, as I say. We took a week's run, a sample every day, and of course some of them naturally had to stand for 7 days. We then mixed these samples and worked on the mixed resultant, and I personally would not like to accept that as a fact, that that lost percentage that we might under certain circumstances take out of the bark, was not available. I believe it is.

MR. YOCUM: Mr. Kelly, have you attempted in any way to figure your losses by wastage in your tail handler, our leakage, etc., and to account in your leaches for that which you claim?

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MR. KELLY: I am not speaking of the efficiency of the tannery.

MR. YOCUM: No, but I am speaking about the ultimate result, in accounting for it.

MR. KELLY: Mr. Chairman, I am not speaking of the efficiency of the tannery, but I am speaking of tannin, soluble, available tannin, so far as hide powder takes it out of the solution, in the analysis of the liquors.

MR. YOCUM: Then you criticise the method of determination. You have either got to take one stand or the other. You can find but a certain proportion of the tannin combined or uncombined in your leather. You know what your losses are in the tan yard. You have either got to say that the method is wrong, or else you have got to say that your presumption is wrong.

MR. KELLY: Well, I have not been a member of this Association long enough to know whether there is a consensus of opinion among all of the members that the official method of analysis with hide powder, using distilled water and everything most favorable to the absorption of tannin is identical with practice in the tannery. I rather think not.

MR. YOCUM: Mr. President, I rather think that what Mr. Kelly has said is brought up from another point of view. I rather think that this data would indicate that the method of analysis, as now outlined, gives us a fair measure of the liquor's value, not only, as some one has objected, because of it being analyzed, say in a 3 deg. liquor, but it represents condition in a 40 deg. liquor. I feel that Mr. Kelly's conclusions are not grounded in facts, and I am positive in my own presumption, that our present methods of analysis do really give us an indication in a fair measure of what goes on in the tannery.

MR. HURT: There is one point where I would like to suggest that both of the gentlemen, Mr. Balderston and Mr. Yocum, might be right. You take an extraction of oak bark, for instance, with an ordinary hard water. While the salts in the hard water are supposed to be insoluble, there are certain conditions, and particularly in the leach house, where I know that the salts are absolutely soluble in the liquors. That does not mean at all that when those liquors go to the yard, and a certain amount of

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acid is absorbed by the hide, that the salts then become unavailable or insoluble. I have seen oak liquors taken direct from the leach house which when concentrated to contain 50 per cent. of solids, would contain a very surprising amount of ash, showing that the salts from the water combined with the tannin, is soluble in the leach house. Of course they become insoluble on the yard. Therefore, Dr. Balderston would find all the tannin in his bark, and at the same time that would not be available for tanning purposes.

(The discussion which followed the reading of Mr. Alsop's paper on the determination of insolubles is related to what precedes, and an abstract of it is here inserted. The paper was read after Mr. Yocum's. It was pubished in the November, 1913, JOURNAL.)

Mr. Reed and Mr. Yocum asked whether the higher insolubles shown in strong solution (see page 466, Nov. JOURNAL) were a loss of tannin as compared with the analysis solution. Mr. Alsop replied that the loss makes the tannin figure as ordinarily determined, lower, and therefore may be regarded as a loss of tannin.

Mr. Yocum expressed a wish that the Council in assigning committee work should take this matter up, with the purpose of determining whether the losses in question are tannin or non-tannin or both.

Mr. Alsop stated that the insolubles in strong solution are always or at least almost invariably greater than in the analysis solution.

C. R. Oberfell asked Mr. Yocum at what strength he analyzed the liquors extracted from the spent material in his experiments Mr. Yocum replied that it was ordinarily less than 1° barkometer. Mr. Oberfell asked whether the difference in strength of liquor in the analysis of new and spent materials might not account for some of the discrepancies. Mr. Yocum thought not. He expressed the opinion that the more a solution of tannin is diluted, provided the tannin is perfectly soluble,* the more tannin is thrown out by ionization.

*** The variable degrees of solubility of different fractions of the tannin of certain materials may be the cause of much of the difference in the percentage of insolubles found at different concentrations.—ED.**

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Mr. Reed suggested that if the tannin is a glucoside it would be absorbed as a whole, and that if the (glucoside) tannin on passing into the tannery should be partly split up, a loss would occur. Mr. Yocum said he questioned whether any glucosides pass into the coolers from the leach house. If the tannin exists in the original bark or wood as a glucoside, it is broken up, liberating the acetic acid that is present in fresh liquors, and passes into the tannery as tannin in the acid condition. Mr. Reed said that in working over G. A. Kerr's method for the detection of mangrove, he had occasion to determine whether or not the tannin of mangrove is a glucoside, and concluded that it is. The test was made on an extract. Hydrolysis converted the tannin, separated by the lead method, into sugar.

DETERMINATION AND ESTIMATION OF TANNING MATERIALS IN ADMIXTURE.*

By F. H. Small.

Mr. President, when I received the notice that I was to be chairman of this committee, and saw the list of names of those who had been assigned to the committee, I was rather elated, figuring that I had more or less of an all-star cast and that there would be a chance for some excellent work, so I sent letters to the various members making inquiry as to the best lines to be followed, only to find that every last one of my all-star cast had a perfectly good reason why he would be unable to do any work this year. My committee report is therefore like the chapter on the snakes in Ireland: "There ain't none."

However, after hearing Mr. Kerr's paper on "The Determination of Mangrove in Admixture with other Tanning Materials," at the last meeting, I have no doubt that many of us went home and instituted experiments along the lines suggested by him, and while we may not have any committee report, it seems to me the subject is sufficiently interesting so that a recounting of experiences may be helpful. I shall be glad to give you a brief resumé, as I see it, of the work that has been done, telling you something

* Report of 1914 Committee, at the Eleventh Annual Meeting A. L. C. A., Chicago, October 28, 1914.

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of my experience, in the hope you will return the compliment and tell me and the rest of us here something of what you may have done.

Mr. Kerr's method, as you remember it, left the test on the basis of a color determination,—that is, the tanning extract was digested with hydrochloric acid, distilled, and the distillate treated with phloroglucin. Ordinarily a greenish black precipitate, essentially furfurol phloroglucid, was produced but mangrove gave a reddish brown precipitate, essentially methyl furfurol phloroglucid. It at once is apparent that the test in this form is open to the objection which holds with regard to all tests depending upon a judgment of colors, and while Mr. Kerr himself made a very fair estimate of the composition of the samples which Mr. Reed submitted to him, those of you who tried to duplicate the work in your own laboratory probably found it a very difficult matter to do so with any kind of accuracy; at least that was my own experience.

Shortly after our meeting, the paper by van Gijn and van der Waerden was published. They showed that methyl furfurol phloroglucid being soluble in alcohol, a separation of it from furfurol phloroglucid, which is insoluble, is possible; so that if it had transpired that all other materials than mangrove yielded the furfurol derivative and mangrove alone gave the methyl derivative, a fairly sharp means of separation should have resulted.

In the case of sulphited extracts they found that the method did not work very satisfactorily, although they suggested that by giving a preliminary treatment with iodine the extract could then be brought into a form where a distillation process would yield more or less of the furfurol and methyl-furfurol that was possible of production.

Next came the paper by Reed and Schubert in which they showed, among other things, that the composition of the distillate varies with the method by which the extract under test is made. That is, a mangrove extract made by cold extraction alone gives apparently almost wholly the methyl-phloroglucid and the red brown color. According as the extraction is made more drastic less and less of the methyl derivative is obtained and more of the furfurol, until when very drastic extraction is used, a straight

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greenish-black color, apparently a wholly furfurol derivative is yielded by the mangrove.

Further than that, they found that a quebracho extract, made by cold extraction, gives a distillate product which is essentially red-brown, the same as that from mangrove, and which is a methyl-furfurol derivative. Now, if the way in which mangrove and quebracho are extracted governs almost entirely the relative amounts of methyl-furfurol and furfurol that are obtained in the distillates from the extracts, we can hardly hope, by the use of this method to distinguish between mangrove and quebracho.

Still later, Moeller, in a paper on this same general subject, calls attention to the fact that the decomposition of the pentosans which are the source of the furfurol, may just as well take place during the manufacture of the extract as later on in the laboratory;—that is, there are organic acids present in the usual tan liquor, and these organic acids, when the liquor is concentrated, may and do act on the pentosans, converting them over to furfurol, which being fairly volatile is driven off to a considerable extent in the process of condensation in the pan.

That being the case, it follows still further that we cannot look for definite yields of furfurol from any particular material. From reading the published work it would appear therefore that the method is far from reliable and has an extremely limited field of usefulness.

Now as to my own work.—I felt that if the ordinary commercial extracts were sufficiently uniform in their behavior under the method, it might still have some usefulness even though all the objections which were brought forward, were true. I therefore took a series of mangrove extracts and a series of quebracho extracts and subjected them to the procedure outlined in the paper of van Gijn and van der Waerden, treating the final precipitate with alcohol in order to differentiate between the furfurol and the methyl-furfurol. I found in the first place that there was no uniform relation between the amount of precipitate and the amount of extract distilled. There was no relation between the total solids or the non-tannins or any other item of the analysis, and the amount of the phloroglucin precipitate. In the case of sulphited extracts, I found that the treatment with iodine was

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worse than useless. Moeller suggests that the furfurol products are absolutely destroyed by sulphiting. My work seems to substantiate this, inasmuch as in practically every case tried sulphited extracts gave a smaller precipitate weight after refluxing with iodine than before.

Another thing, the amount of the precipitate from any given material which is soluble in alcohol is variable. In the case of mangrove extracts, practically all which I tested and which included about all that I could find on the market, gave a solubility figure of essentially 100. That is, in practically every case the whole of the phloroglucin precipitate went into solution in alcohol.

In the case of quebracho, however, the solubility figures varied decidedly, from practically nothing up to as much as 50 per cent. It is then manifestly impossible to take a mixture of mangrove and quebracho and state that a supposedly pure quebracho has mangrove in it because a percentage of the phloroglucin precipitate is soluble in alcohol.

In one case where this method might be used it seems that it may have some real merit. No hemlock extract that I have tested has shown a solubility figure as high as 5 per cent.,—that is, no hemlock extract distilled with hydrochloric acid, phloroglucin added to the distillate and the precipitate digested with alcohol showed a precipitate solubility as high as 5 per cent. If, therefore, you meet a hemlock extract which yields a precipitate more than 5 per cent. of which is soluble in alcohol, I believe you will be justified in claiming that the hemlock extract contains some material other than hemlock,—this material being very possibly mangrove.

I tried some mixtures of hemlock and mangrove in an attempt to discover whether quantitative estimation of proportions was possible, but as might be expected, found only rough approximations obtainable, owing to the variable weights of the precipitates from both mangrove extract and hemlock extract

That covers roughly the work done. I will do what I can to answer any questions you may wish to ask me about it, or any details that I have not explained. Personally I should be very glad indeed, to hear the experience of any of you along these lines.

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DISCUSSION.

MR. ALSOP: The subject is open for discussion.

MR. REED: I would like to ask Mr. Small whether he tried any tanning materials other than mangrove and quebracho and hemlock. Did he try black oak bark?

MR. SMALL: No, I did not; I tried some of the other commercial tanning extracts like chestnut and myrobalans, but not black oak bark.

MR. REED: Black oak bark will give it, according to my tests. True cutch will give it also.

MR. SMALL: I don't know what the price of true cutch is, but I suppose it to be a fairly expensive material, and one not likely to be used for the purpose of adulteration. What I was looking for was help in detecting some of the more common adulterations.

MR. REED: I think that Mr. Kerr stated last year in his report upon this matter that the reaction in the case of mangrove was one of the non-tannins; that it is a function of the non-tans, and that it could be gotten from the non-tans. Tests that were made in our laboratory proved that this was not true. It is altogether a function of the tannins. I think I am right in my statement that Mr. Kerr said that it was the function of non-tannins.

MR. PEIRSON: We have worked on this in the laboratory at Smethport, and I can substantiate everything that Mr. Small said. In no case do we find solubility of the precipitate in absolute alcohol more than 5 per cent., and sometimes it does not average more than between 4 and 4½ per cent.

REPORT OF COMMITTEE ON MISCELLANEOUS METHODS.*

By L. Balderston.

The particular topics mentioned in the instructions given to this committee were lactic acid and the materials used in the manufacture of chrome leather. Some collaborative work has been done on the second topic, but none on lactic acid. The chairman has had too little experience in the analysis of this acid

* Read at the Eleventh Annual Meeting, A. L. C. A., Chicago, Oct. 28, 1914.

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to be able to assign work with any certainty of its appropriateness or value.

The last published work on the analysis of lactic acid by a member of our Association of which I find any record in the JOURNAL, is by W. H. McLauchlan, in the January number, 1907. The title of this paper, which was presented at the third annual meeting in November, 1906, is "The Determination of Volatile Acids in Commercial Lactic Acid." The author concludes from a series of careful experiments that lactic acid volatilizes on the evaporation of dilute solutions, the amount depending on the temperature and the rate of evaporation, that the loss cannot be accounted for by the formation of anhydride, and that the amount evaporated is proportional to the strength of the solution.

An article on "Lactic Acid in America," read by the same author before the Seventh International Congress of Applied Chemistry, 1909, appears in the JOURNAL for September of that year.

In the April number, 1906, is a paper by Dr. M. Philip, translated from *Collegium,* on the analysis of commercial lactic acid. He calls attention to the tendency of concentrated solutions to go over into anhydride by the splitting off of a molecule of water from 2 molecules of acid and recommends titrating for free acid, then adding excess of sodium hydroxide, boiling, and titrating back with acid. This method, which is the same as that given in Procter's "Leather Industries Laboratory Book," has since been shown to give high results, supposed to be due to the using up of alkali by impurities present in the acid. Dr. Besson, an abstract of whose work is given in the JOURNAL for April, 1910, page 231, finds that the anhydride is all taken up by letting the vessel stand 10 minutes in the cold.

The various writers on the subject do not agree in regard to the method of computing anhydride after the titrations are made. Procter distinctly says that if the first titration be done quickly the anhydride is not affected, and the result of this may therefore be taken as free acid. Philip in the article already mentioned, says that the anhydride enters into reaction with the alkali, and so uses half as much hydroxide as an equivalent amount of acid, since 1 molecule of anhydride is the product

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of decomposition of 2 molecules of acid. The amount of anhydride shown by the difference in the two titration figures would thus be only half of that present. The same view is taken by Klapproth, November JOURNAL, 1911, page 527, and as Besson in a criticism of this article (see January, 1912, JOURNAL, page 48) makes no allusion to this point, I infer that he makes his calculation in the same way. The method used by Harrison Brothers, Philadelphia, assumes that the result of the first titration gives free acid. Which view is correct the present writer is entirely unable to decide. Another point intimately connected with this is the deliming effect of the anhydride. Procter says it is supposed to be valueless for this purpose. Other writers, including Besson, do not agree that the anhydride does not combine with the lime of the hide, and here again, further light is to be desired.

Since lactic acid is generally made by decomposing calcium lactate with sulphuric acid, free H_2SO_4 must be looked for. Dr. Philip, in the paper quoted, recommends for free sulphuric acid the following: (1) determine total SO_3, (2) determine SO_3 in ash, (3) determine ammonium sulphate by means of an ammonia determination, then subtract the sum of the second and third amounts of SO_3 from the total. Tests should also be made for hydrochloric acid, oxalic acid and iron, which, if present, may be determined by well known methods.

It would seem that a method for the examination of commercial lactic acid should concern itself chiefly with 3 things, (1) free sulphuric acid, (2) lactic anhydride, and (3) volatile acids. The method used by Harrison Brothers & Co. for free sulphuric acid is based on the insolubility of sulphates in alcohol, and is as follows: To 50 grams of the acid to be tested add 200 cc. alcohol, 96 per cent. Heat on steam bath 2 hours, and let stand in warm place 12 hours. Filter off the precipitated sulphates and wash with alcohol. Evaporate filtrate till free from alcohol. Add hydrochloric acid, boil, precipitate free sulphuric acid with barium chloride.

Besson's method for lactic anhydride is probably dependable. He titrates with alkali, and phenolphthalein, adds excess alkali, lets stand in the cold 10 minutes, adds excess acid, boils, and

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titrates back with alkali. The purpose of boiling with acid is to decompose carbonates formed during standing.

The greatest difficulty in the lactic acid problem seems to be the matter of determining volatile acids, of which several may be present in small quantities. It may be practicable to work out an empirical method which will give results close enough for practical purposes. Having determined free sulphuric acid, total acidity and lactic anhydride, it would be necessary to get a figure for volatile acids, and then the free lactic acid would be the difference between the total acid and the sum of the other three. For the determination of the volatile acids, the method of successive distillation has been used with fairly satisfactory results, following some such scheme as this: Take 2 grams of the acid to be tested, dilute to 100 cc., distil off 80 cc., make up to 100 with water and again distil off 80, and so on for 4 distillations. Then titrate the added distillates for volatile acids, and express in terms of acetic. Mr. McLauchlan has shown that by this method some of the lactic acid comes over, but it is possible to so standardize the process, in the matter of rate of distillation, strength of solution, etc., as to get results pretty close to the truth. I believe that this may be cut down to one distillation, multiplying the acid found in the distillate by a factor determined by a careful series of experiments. By making up solutions containing the same known percentage of pure lactic acid and varying percentages of the different volatile acids, and distilling these mixtures under carefully controlled conditions, I think it will be found that a table may be made which will enable us to find the proportion of volatile acid with approximate accuracy.

Another subject assigned to this committee was the matter of analysis of chrome leather and its raw materials. The chairman prepared a sample of chrome leather, put up 50 grams each in sealed bottles, and sent to Messrs. Levi, Evans and Kernahan. Directions requested moisture determination and duplicate determinations of chrome by each of the two methods described in Levi and Orthmann's paper in the July JOURNAL and by Procter's second method. These are designated as 1, (sodium peroxide, described below), 2, (carbonates and borax glass, described below), and 3, (Procter.) Procter's second method is to mix the

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ash of 3 grams of leather with a mixture of magnesium oxide and sodium carbonate, heat to a white heat in a platinum crucible 30 minutes. When cool, dissolve in hot water with enough HCl to make the solution acid. Filter. Treat again any undissolved residue by ashing the filter and mixing the ash with a fresh mixture and heating again. Add the 2 solutions. Make up to 500 cc. To 100 cc. add 5 cc. of hydrochloric acid and proceed as in the case of chrome in chrome liquors (below). The results of analyses are shown in the table, figures being percentages.

	Moisture	Method 1	Method 2	Method 3
A. C. Orthmann.....	17.4	4.53	4.53	4.53
C. M. Kernahan.....	14.9	4.47	4.47	4.43
		4.52	4.39	4.47
J. E. McNutt.....	16.8	4.54	4.52	—
		4.50	4.54	—
L. Balderston	17.5	4.56	4.60	4.56
		4.52	4.60	4.56

The collaborators agree in recommending method 2, which converts all the chrome into chromate with a single fusion. When chrome only is wanted, 1 is satisfactory, requiring a short time for the fusion.

The collaborators had not tried the Tarshis method, described in the June JOURNAL. The chairman has made further efforts to substitute potassium chlorate for nitrate in this method, but without success. He believes it will hardly find wide application because it is generally necessary to determine the ash, which Tarshis method does not permit.

All the members consulted approve of the methods for chrome and acid in chrome liquors given in Procter's Leather Industries Laboratory Note Book. These methods are detailed below.

For the determination of chrome in bichromates Mr. Orthmann prefers to take a larger sample, say 100 grams, dissolve it, take an aliquot part of the solution and again dilute. For the sodium bichromate in fine crystals the chairman has found 5 gram portions from the same sample to give very uniform results.

Among the many determinations for which we should have a recognized method, one which has claimed attention in the Ridgway laboratory is the determination of iron in extract. We are using a colorimetric method which is reasonably satisfactory, but it takes too much time. We have spent a good deal of time trying

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to work out a practicable titration method, but so far without success.

Recommendations.

Lactic Acid.—Collaborative work should be done to test known methods for free H_2SO_4 and for anhydride. Efforts should be made to work out a method for estimation of volatile acids from the result of a single distillation carried out under specified conditions.

Chrome Determination.—It is recommended that the methods of the L. I. L. B. for chrome and acid in liquors, and the two methods for chrome in leather described by Levi and Orthmann in the July JOURNAL, be incorporated in our printed methods. These are herewith given in detail.

Chrome in Chrome Liquors.—Dilute the liquor so that it contains from 0.15 per cent. to 0.25 per cent. of Cr_2O_3. To 10 cc. of this dilution in a 300 cc. Erlenmeyer add about 50 cc. of water and about 2 grams of sodium peroxide Boil gently 30 minutes. Cool. Neutralize with strong HCl and add 5 cc. excess. Cool again. Add 10 cc. of a 10 per cent. solution of potassium iodide. After 1 minute run in N/10 sodium thiosulphate until the iodine color has nearly disappeared. Add a few cc. of starch solution, 1 gram per liter, and titrate to the disappearance of the blue. One cc. N/10 thiosulphate is equivalent to 0.002533 gram Cr_2O_3.

Acid in Chrome Liquors.—Place 50 cc. of the above dilution in a 7-inch porcelain dish, add 400 cc. water and 1 cc. of a 5 per cent. solution of phenolphthalein. Bring to a boil. While boiling, titrate with N/2 NaOH until the pink color persists after 1 minute boiling. One cc. N/2 NaOH is equivalent to 0.02452 gram H_2SO_4 or 0.01823 gram HCl.

Chrome in Chrome Leather.—(*a*) Ash 3 grams of the leather. Mix the ash well with 4 grams of a mixture of equal parts of sodium carbonate, potassium carbonate and powdered borax glass, and fuse for 30 minutes. Dissolve the cooled fusion in hot water with enough HCl to make an acid solution. Filter. If there is any residue on the filter ash it and treat the ash with 1 gram of the fusion mixture in the same manner as the original ash, adding the solution to the first. Make up to 500 cc. To

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100 cc. of this solution in an Erlenmeyer add 5 cc. HCl and proceed as above.

(*b*) If it is not desired to determine Al or Fe the ash of 3 grams of leather may be transferred to an iron crucible, mixed with 3 grams of sodium peroxide and fused 10 minutes. Place cooled crucible in 300 cc. water in a casserole and boil 20 minutes. Wash into 500 cc. flask, cool and make up to the mark. Filter 100 cc., place in Erlenmeyer, neutralize with HCl, add 5 cc. excess and proceed as above.

DISCUSSION.

T. A. FAUST: I think it is very important that we have some way of telling the volatile acid in a sample of lactic acid. These acids are sold on a percentage basis, and we ought to find some way of protecting the purchaser. We have found the method to be reliable, of taking the titration direct to phenolphthalein, and deducting from that the acetic acid. To determine the acetic acid we take 100 cc. and distil off 90 and titrate, distilling rather slowly. Eachus did some work about 5 or 6 years ago, and he found that in samples of C. P. lactic acid a slight amount of acid is distilled over. And as we lose a little of the lactic acid in our distillate, I believe that the errors compensate for each other, and that the one distillation is sufficient. Another thing, we found it necessary to test for hydrochloric acid and phosphoric acid.

In answer to a question by H. C. Reed, L. Balderston explained that if the amount of volatile acid is to be found from a single distillation, it would be necessary to make a table showing what percentage of volatile acid corresponds to each quantity of acid distilled over from a definite quantity of the dilution of the original acid used for analysis. The table would be on the same plan as the Munson and Walker and other tables showing the relation between reduced copper and glucose.

Dr. Rogers asked whether anything had been done in regard to a method of stating the basicity of chrome liquors, and received a negative answer.

MR. ALSOP: Wouldn't this table for volatile acids depend on the kind of volatile acid present?

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MR. BALDERSTON: That is a question, and I presume it would. I do not think the percentages of volatile acids present would vary so widely as to make the construction of such a table hopeless.

MR. YOCUM: Mr. President, I should say that where the amount is so little, as it is under ordinary distillation processes as outlined, if the volatile acid were acetic acid only, no table would be necessary. I remember when we used to distil 100 cc. or 125 cc. and called it 80 per cent. of the total acid, which was so nearly accurate that tables were unnecessary. If such procedure could be adopted on this lactic acid, it would determine volatile acids in a manner accurate enough for all purposes.

MR. REED: I think that what should be determined is the value of the lactic anhydride. That is, some knowledge of how valuable it is, or something to that effect. I don't think we know.

MR. BALDERSTON: That would be a separate problem.

MR. REED: I know, but we need it.

MR. BALDERSTON: We need it, there is no question about that. It is a practical thing.

MR. FAUST: It ought to go into the methods; it is practical. We don't do that at present, and I don't think it is available, but some of the manufacturers claim it is available, and some of them are very anxious that we report on that.

THE BATING OF HIDES AND SKINS.*

By Allen Rogers.

I am not prepared to give any set address on "The Bating of Hides and Skins," but as my name appeared on the program I thought possibly I might take a few minutes and just talk informally in regard to this new unhairing and bating process which we have seen mentioned in the scientific and the trade journals recently, known as the Ara process, which unhairs and bates in one operation. This material is prepared by a German company and through their courtesy I was able to get a small amount of it for experimentation. I have a little bottle in my

*Address at the Eleventh Annual Meeting, A. L. C. A., Chicago, October 29, 1914.

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pocket, and will pass it around, so that you may see some of it. This is the product made from the pancreas, which contains unorganized enzymes or unorganized ferments. The method of using this material is in the experimental stage, as yet, and the company that controls it does not offer it for sale. But the way it works is quite interesting, and if you have not seen it work, I thought perhaps you might care to.

In working with it a fairly long treatment is suggested and in those tests that I carried on at the start I got a very pipey, and very flat piece of leather, as I gave it quite a lot of time. Finally I cut down the time quite a bit and changed the method of treatment, until the method that gives me the best result is to soak the skins in the ordinary way, and then place them in the paddle in a tenth of 1 per cent. solution of caustic soda over night—that is a tenth of 1 per cent. of the weight of the water. This plumps the skins so that they are in the same condition as limed stock. At the end of 24 hours the caustic solution was drawn off and the paddle again filled with water, at about 90° F. with enough sodium bicarbonate to correspond to a tenth of 1 per cent. solution. The stock was run for about 15 or 20 minutes and then one tenth of 1 per cent. of "arazym" added.

The method I use now is to treat with the caustic soda, put in the bicarbonate and the arazym, and in 24 hours practically all the hair is off. At the end of 24 hours more they are completely unhaired, and the stock then is in a flat condition, just the same as you would take it out of a manure bate, or any other kind of bate. Last week I ran some kangaroos. These kangaroos were brought over from a tanner in Newark. They were plumped for 24 hours, and put in the arazym. At the end of another 24 hours, after adding the arazym they were completely unhaired.

You don't lose the hair with the arazym, which is a very important item. The hair is silky, and it can be handled with a common manure fork. Of course it can be washed too.

DISCUSSION.

MR. WALLIN: Does it get the hair loose?

DR. ROGERS: Yes. And then you put it in a drum and mill it. It might be well to scud it.

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This is a piece of skin on which they have been making some experiments here in Chicago, and they cut off a piece and sent it up to me. I don't know whether you want to hand this piece of skin around, but you can see this is white hair. Here is the hair as it comes off. This is all ready now to take out, and it leaves the stock in a nice, soft condition. Here is a piece that is not quite finished. I will pass some of the hair around to show the condition of the hair; it is nice and soft and silky. And I think that it promises to be of interest to the tanner.

MR. WALLIN: Doctor, you said the hair was entirely removed. Do yo mean without any mechanical operation?

DR. ROGERS: Yes, the hair is removed without any mechanical operation.

MR. WALLIN: All off from the hide in the vat?

DR. ROGERS: Yes. At the end of 48 hours in the paddle the skin is smooth. And very little beaming is necessary. Once in a while on the flank you see a little piece that requires beaming, but it is practically all off in the paddle, and it settles in the bottom of the paddle.

MR. WALLIN: You beat it off in the paddle?

DR. ROGERS: Yes, beat it off in the paddle. Paddling around in the paddle beats it off. If it is not all off then you can put it in the mill, or if you want to you can work it on the beam and scud it. The skin, if you notice, too, is already bated.

Now as I said on the start, we obtained some very pipey leather, and some flat leather, but that is when we used the longer treatment, and since we are cutting down the time the skins are much tighter.

Here is a piece of cow hide, some sheep and some goat skin. Here is also a picee of sole leather that was treated by the process. In regard to its application, if it should ever be of any use, it would be in light stock, calf and goat. It worked very beautifully on calf skins and sheep skins. It would be probably all right on side leather that you were going to split. In the case of sole leather I don't think it would be applicable. Automobile leather would be all right. In fact, any kind of leather that you wanted in a bated condition. In the case of sole leather you don't want it bated.

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MR. V. N. HAMANN: How is the material prepared?

DR. ROGERS: They do not say. And I do not know what it is going to cost, except that it is estimated that it ought not to cost as much as the present process. It ought to cost about as much as bating.

MR. HAMANN: How long does it take on a skin, for instance?

DR. ROGERS: The quickest test that I made was this test of last week on a kangaroo, and that was 48 hours; that is including the plumping and the unhairing. Ordinarily it takes 3 days.

MR. HAMANN: There is no advantage over straight sulphide then?

DR. ROGERS: Yes, because you have the salable hair, which in the case of sulphide is lost, and it costs a great deal more to bate.

MR. HAMANN: You would not bate on a straight sulphide?

DR. ROGERS: Well, for calf and goat and sheep I don't think very many people would be sulphiding and not bating; very few people do that. They usually bate. And as to the cost, I don't know anything about it, excepting that the makers said that it would not cost more than bating.

Another thing: You are speaking of this business of liming and sulphiding. It means that you practically eliminate the beam house, and then all the work these people have been doing on the sewage will not have to be done. You won't have any sewage to look out for.

One thing about it that possibly may be an objection is that after this stuff has been running for 2 days it has, what you might call a fairly unpleasant odor. It gets quite ripe. But if you don't mind that it is all right. Of course that is not really objectionable. After you get used to it you can sit down and eat your lunch by the side of it, but if you don't run it too long there is no trouble on that score.

MR. BALDERSTON: You don't have to renew it?

DR. ROGERS: No. They recommend that you use the old liquor. Take your stock and plump it with the caustic soda, and throw it into an old liquor for reducing the swelling, and let it run there for an hour, and then throw it into your new arazym. It saves in cost and material.

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Another thing, in the first experiments I used two-tenths of 1 per cent. solution, and finally cut it down to one-tenth, and got just as good results. So that means a pound in 1,000 pounds; a little less than a pound to 100 gallons, which is about the same concentration that you use in the bate.

MR. VEITCH: I would like to suggest that you leave it out entirely and see what would happen.

DR. ROGERS: Well, as a matter of fact, you can unhair and bate and paddle and tan and color all in one day if you are in a hurry, but not with this product. I don't know of any questions that I can answer; as far as the chemistry end of the matter goes I am not able to tell you anything.

MR. LUMBARD: Have you unhaired heavy hides?

DR. ROGERS: Yes, unhair heavy hides in just the same time that it takes on light stock. On the heavy hide I don't hardly think it would be of so much value, because in the case of a heavy hide, you want to get plumpness, and you don't want your stock so free from lime when it goes into your liquor. I got some very good results in a chrome combination, and in that case you do want the lime out of it, and it worked very well then.

MR. ORTHMANN: Does it plump easily after you take that out?

DR. ROGERS: Yes, after you put it in the caustic soda it begins to plump in 2 or 3 hours. In fact, a great many people hasten the time of soaking by adding a little caustic soda. You can cut down the soaking, and I have done that with some skins, we ordinarily soak 3 or 4 days. That is soak it 1 day, and put in $^1/_{10}$ per cent. solution of caustic soda, and the next day they are ready to mill, then go ahead and treat with arazym or lime or anything else so taking 2 days in soaking and 2 days more in unhairing and bating, why by the time you would ordinarily soak the stock it would be unhaired, bated and tanned.

MR. HAMANN: What is the action of this product on dry hide as compared with green hide?

DR. ROGERS: I have not noticed any difference. You see you bring the dry hide up to practically the same condition as

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you would green hide, and then when you come to unhair I don't see any difference. I will leave this sample on the table here, and you can examine it if you wish.

DISCUSSION OF THE REPORT ON FORMS FOR REPORTING ANALYSES.

(The report was published in the JOURNAL for November, 1914. The discussion, an abstract of which follows, took place at the Chicago meeting on Oct. 28, 1914, when the report was presented.)

F. P. Veitch thought it a good plan for the Association to adopt definite forms of report for the usual analyses. He expressed the opinion that it would be well to take barkometer readings at the standard temperature as far as possible, and so avoid the necessity of corrections.

C. R. Oberfell remarked that one of the important reasons for the use of a barkometer correction table is to enable the chemist and the liquor runner to agree in their readings, and it is out of the question for the latter to cool his liquors to 60 deg. in order to take a reading.

J. H. Yocum corroborated Mr. Oberfell, and said further that there is an inconsistency in using 60° F. as the standard temperature for liquors when we make our analyses at 68. He was of the opinion that corrections at temperatures above 100° F. are liable to considerable error. He mentioned the work of Dow on this subject in 1896 or 1897. Dow went into the matter very fully, and it would be worth while to try to get the report of his work.

Mr. Veitch remarked that the precipitation which takes place in many liquors on cooling would seriously interfere with the accuracy of any correction applied to the barkometer reading of a hot liquor.

T. F. Mosser said that the matter of half or quarter degrees is not material, and it will be found possible to get out a table that will give the correction to within 1 deg. for all necessary temperatures.

T. A. Faust asked how closely the four tables submitted to the

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committee agreed. Mr. Alsop replied that three of them were in good agreement, and the fourth was a little different.

F. H. Small reverted to the earlier remark of Mr. Yocum that the standard temperature for barkometer readings ought to be higher than 60 deg. He said he was using some specially made barkometers which were standardized to 70 deg. Seventy deg. is a good average temperature for yard liquors, the year round. If the barkometer was standardized at 70 deg., the variations would not be great enough to make any serious error in the correction likely to occur. He saw no real reason for continuing to use 60 deg. as the standard temperature, as it is simply a relic from old-time laboratory practice, when it was customary to work at 60 deg. Since it is the practically universal custom in this country now to work at 20° C. (68° F.), it would be only logical to have our apparatus standardized at that temperature or one very near it. Mr Small thought it desirable to have standard forms which members of the Association should use in making reports. Beside tending to uniformity, this would be of some assistance to the tanner in interpreting reports. Provided all the data generally called for are included, the arrangement of the form is not a matter of profound importance. The speaker preferred a form in which the analysis would be so arranged as to add up to 100 per cent., that is to say, form No. 2 in the report for extract analysis. He favored putting the matter in the hands of a committee to draw up forms for the materials which leather chemists are called on to analyze, and when the forms shall be agreed on, the use of these forms by all members, at least in commercial work.

C. R. Delaney inquired of Mr. Alsop whether it is customary to determine the specific gravity of extracts with a hydrometer or a pyknometer. Mr. Alsop said he was unable to answer the question. Mr. Delaney favored the pyknometer method, as he believed hydrometers to be liable to change with lapse of time.

Dr. Rogers suggested that when uniform reports are adopted, the blanks should be made of uniform size by all chemists, to facilitate filing by the recipient.

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DEALING WITH ANALYSIS IN CONNECTION WITH BEAM HOUSE PROCEDURE.*

By Dr. Allen Rogers, Chairman.

DR. ROGERS: When I was appointed on the Committee, together with one of our associates, we went to work on this problem, and one of the difficulties we encountered was the determination of hide substance in unhairing liquors. A number of methods have been proposed for it, some of which are control methods only, and others seem to be accurate methods. We have taken these methods and tried to get some checks between them, such as the Kjeldahl determination, the methyl-orange indicator determination, and also the formaldehyde, but with these three methods we did not seem to get concordant results. Between the formaldehyde, the methyl-orange and the Kjeldahl determinations, we do get better results with the two latter than with the formaldehyde. With straight lime liquors we do not get such good results, as most lime liquors contain sulphide, and we encounter more or less difficulty, and on that account we are working to get something definite to propose, and then I want to come back to the secretary and see if we can get some help on it.

But at first it seems to me the best thing to do is to get something definite to work at before asking for help from any of the other members of the Association. We are now taking known samples and trying to see if we can in some possible way devise a method, either a combination or possibly a new method, that will work out and give us better results. In the determination of lime, soluble lime, available lime and sulphide, there is no difficulty at present. But the control work probably rests more on the hide substance that we find in the lime than anything else. That is the thing we want to know, how much hide substance has been lost. Of course, we say "hide substance." It may not necessarily be hide substance. It may be albuminous matter. And we want to remove that, but of course, whether we can distinguish between albumen and gelatin I am not prepared to say. But if in our control work we can say that there is so much hide substance, and state it absolutely, then I think we will have

* Report presented at the Eleventh Annual Meeting, Chicago, October 28, 1914.

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something that will be of help, and that is what I have been trying to do. I should like to continue with this work, and during the coming year we hope to be able to get something that will be of value.

DISCUSSION.

MR. OBERFELL: I would like to ask Dr. Rogers what is the essential difficulty in determining the hide substance by the Kjeldahl?

DR. ROGERS: There is no difficulty as far as Kjeldahl goes, outside of the time it takes, that is all. For control work it would be much better if we had a quick method. The method proposed by Stiasny was to use methyl-orange indicator. Also a lot of work was done by McCandlish. And quite a bit of work has been done by Procter. But what we are trying to do is to see if we can get some quicker method. The formaldehyde method is quick, very rapid, but we do not seem to be able to get the two methods to check. And that is what we are trying to do.

MR. OBERFELL: Did you have any special difficulty in concentrating your lime liquor?

DR. ROGERS: No, I didn't try to concentrate it. We tried to take a definite sample, and then for the Kjeldahl process we filter that off or let it settle, and take the supernatant liquor. Of course, what we want is the nitrogen in solution, and then put it in the flask and run it down. We didn't have any trouble there.

MR. OBERFELL: It runs down all right?

DR. ROGERS: Yes.

MR. OBERFELL: There is a great deal of trouble there from bumping caused by precipitated calcium sulphate.

DR. ROGERS: We didn't have any trouble with that. We usually put in pumice stone, which helps.

MR. FAUST: I would like to ask Dr. Rogers if he did any work to determine the nature of the alkalies. For instance, we have four or five different alkalies present in lime liquor where we are using sulphide, and I would like a method of determining how much caustic soda is in the lime liquor.

DR. ROGERS: When you use lime and sulphide you have some caustic lime and you have caustic soda. In some of the work we did a couple of years ago we did make some separation of that

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in trying to determine the proportion of caustic soda. We determined the causticity by the titration method.

MR. FAUST: A difficulty in computation arises there from the fact that the sulphide is not all there as sodium sulphide. It is there as calcium sulphide and poly-sulphides. You have four or five alkalies there, and you haven't anything to start from.

MR. VEITCH: Mr. Chairman, some papers have been published, and there has been a great deal of discussion on the nature of lime sulphur solutions that might be of interest along the line you spoke of, Mr. Faust, about the nature of the compounds in lime liquors. Those people have been experimenting with the compounds that are in the lime-sulphur solution, and I do not know whether they have got a full list of all that may be and are present, but there are many. They are very interesting papers, I know, and might throw some light just along this line. I think they are published both in the *Journal of the American Chemical Society* and also in the *Proceedings of the Association of Official Agricultural Chemists*, relating to washes for controlling insects and fungus diseases.

NOTE ON PENTOSES.

NEW YORK, N. Y., Dec. 16, 1914.

THE EDITOR OF THE JOURNAL A. L. C. A.,
Ridgway, Pa.

DEAR SIR:—

On reading "Further Coommunication on the Determination of Pentose in Tanning Materials," by J. L. van Gijn and H. van der Waerden, in *Collegium*, No. 531, we note that the authors attribute several erroneous statements to us.

Messrs. van Gijn and van der Waerden interpret one of our statements as follows: "The remarks of Reed and Schubert in reference to the decomposition of rhamnose on heating 4 hours at 4 atmospheres are only confirmed in part by us; 200 mg. rhamnose still give according to this test (HCl distillation) 119 mg. phloroglucid instead of 125 mg. given by distilling the untreated rhamnose."

On referring to our paper (JOURNAL, A. L. C. A., 1914, page

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134) Messrs. van Gijn and van der Waerden will find that our statement is as follows: "It was thought possible that the methyl-pentoses might be split up into pentoses under the influence of temperature and pressure, and tests were made by employing method 3 (pressure extraction, 150° C. sealed tube, 4 hours) on a solution of pure rhamnose, but on distilling with acid in the usual manner no furfurol test was given by the distillate."

When pure rhamnose is distilled with hydrochloric acid, one of the products is methyl-furfurol (no furfurol or only a small amount due to impurities in the rhamnose).

If Messrs. van Gijn and van der Waerden will refer to our paper they will find that we state that rhamnose gives no test for furfurol when heated under pressure.

As pentose sugars give a powerful furfurol test, it is plainly evident that rhamnose is not converted into a pentose sugar when it is heated under pressure.

Messrs. van Gijn and van der Waerden also state: "Reed and Schubert also claim that by extracting under pressure the methyl-pentoses are converted into pentoses."

On the contrary we stated our results as follows: "From these results we argue that the character and method of extraction has a decided influence on the test. In other words the green or yellow coloration and black, red or brown precipitate depends altogether upon the proportions of furfurol and methyl-furfurol present in the distillate and this in turn depends upon the degree of extraction. Methyl-pentoses or methyl-pentose-forming compounds are apparently more readily extractable from the materials containing them than are pentoses or furfurol-forming compounds."

We are therefore at loss to understand how Messrs. van Gijn and van der Waerden can state that we find the results they quote, our results showing that the amounts of pentoses and methyl-pentoses and in turn the amounts of furfurol and methyl-furfurol obtained on distilling an extract with hydrochloric acid are dependent on the degree of extraction of the fresh material.

In conclusion we desire to state that we are confident of the accuracy of our experiments and that as a distinctive test for

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mangrove extract, the test is of no great value, as extracts not containing mangrove, but giving a mangrove reaction can be easily manufactured. You can also extract mangrove bark so that the resulting extract will react similar to quebracho extract by this test.

Regretting that this difference of opinions has arisen and trusting that it is only due to a misinterpretation of our paper into the German language.

We are

Very truly yours,

H. C. REED,
ADOLF SCHUBERT.

(A full abstract of the article by van Gijn and van der Waerden is given on p. 70.—ED.)

ABSTRACTS.

Hide, Skin and Wool Market in South Africa. G. H. MURPHY, in *Consular Reports.* Under date of Aug. 26, Consul Murphy writes that prices have fallen from ¼ to ⅓ in consequence of unsettled conditions.

Tanneries for West China. E. C. BAKER, in *Consular Reports.* The province of Szechwan produces many hides and skins of good quality. These are sent to foreign markets through three or four hands. The province has no direct access to the markets of the world. The people are awaking to the disadvantages to which this fact subjects them, and are seeking to arrange to ship direct to American and other markets direct from Chungking via steam vessels on Yangtse River. The trade school at Chengtu, capital of the province, will soon be teaching the Chinese to make leather by modern methods, and the opportunity for the sale of tannery machinery and equipment will in all probability soon be presented, as there are capitalists in the region who are aware of the advantage to be reaped from the manufacture of Szechwan hides and skins into leather on the spot.

Modified Kjeldahl Flask for Determining Soil Nitrogen. H. A. NOYES. *Journal of the American Chemical Society,* Vol. 36, p. 2541. The bottom of the flask is more sharply curved than the other parts. Solid matter is thus kept in motion, since heat applied at the tip causes the liquid to boil most vigorously at the point where the solids would naturally settle.

Liége Tannery School. *The Leather World* publishes a letter from Professor E. Nihoul, director of the school of tanning connected with the University of Liége. Professor Nihoul is now at Cardiff, Wales. He reports that the tanning school was at last accounts still standing, but

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that most of the buildings of the University were wrecked. Beside the damage caused by the bombardment of the city, the Department of Industrial Chemistry, he states, has suffered the loss of its valuable collections and instruments, which have been sent to Germany.

The Presence of Chrome Soap in Chrome Leather. G. HUGONIN. *Collegium,* 1914, pp. 716-7. Chrome leathers are generally curried with soap and oil, the object of the soap being to emulsify the oil and enable it to penetrate the hide. According to some, an insoluble chrome soap is formed within the leather, giving it more body and improving its appearance. Impressed by the fact that certain manufacturers use neither soap nor sulphonated oils and obtain leather of as good body as when soap is used, the author was led to investigate the truth of the chrome soap formation. He first precipitated a chrome soap by mixing neutral solutions of soap and chromic chloride. The blue precipitate after washing and drying, yielded a grey powder of 16.5 per cent. Cr_2O_3. It was insoluble in alcohol, very little in ether and petroleum ether, but fairly soluble (6-7 per cent.) in crystallizable benzene. Leather containing this soap should therefore give it up on extraction with benzene in the Soxhlet apparatus. Various chrome leathers were thus extracted, but did not yield a trace of Cr in the extract. Further the examination of the residual soap used in emulsifying a fat liquor for 50 kilos of kid showed no appreciable consumption (5 per cent. by analysis) of soluble soap.

The author is of the opinion that chrome soap is only possible in leather incompletely washed after tannage or partially neutralized and that it is not present in a normally manufactured product.

W. J. K.

(A brief abstract of this work appeared in the number of August, 1914, taken from *Le Cuir.*)

The Determination of Sulphite-Cellulose by Cinchonine. W. APPELIUS and R. SCHMIDT. *Collegium,* 1914, pp. 706-7. The authors supplement their previous article (abstract, ante p. 566) in which they find that all tannin solutions, excepting those of sulphite-cellulose, give precipitates with cinchonine which redissolve on heating. They have since examined two cellulose extracts, one of which gave no precipitate at all and the other much less than extracts previously examined. When tannin solutions were added to these extracts, the reaction described was distinct with copious formation of precipitate. The precipitate of sulphite-cellulose with cinchonine is therefore soluble on heating, but the solution is prevented by even very small amounts of tannin and the characteristic lumpy, brown-black precipitate results. If a sulphite-cellulose extract does not give the cinchonine reaction, it can contain very little ordinary tannins. In the other case when an insoluble precipitate results, several possibilities occur. The sulphite-cellulose can from its nature contain substances which behave like ordinary tans, or tannin may have been added. Sum-

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ming up the directions for the cinchonine test, if sulphite-cellulose is to be searched for, the prescriptions previously given are to be accurately followed. Pure cellulose extracts which do not give the reaction, or but slightly, are given an addition of tannin solution and the test repeated.

W. J. K.

Determination of Wood Gum (Xylan) in Chestnut Wood Extract. LEOPOLD POLLAK. *Collegium*, 1914, pp. 715-6. Xylan is found in most woods and especially in beech. It is not found free in the fiber since it cannot be extracted by boiling water, but is obtained by extraction with alkali and may be considered a hydrolytic product. Acids also liberate xylan even after exhaustion of the wood with alkali. This is important in practical extraction where the xylan is continuously liberated in the acid solution and by its colloidal properties favors decolorizing and clarification.

Xylan was prepared by the author following the directions of Wheeler and Tollens. The wood was first extracted with 2 per cent. ammonia to remove the tannin, then with dilute NaOH, precipitated with alcohol, and the alkaline gummate decomposed with HCl. The xylan obtained was a light brown, soluble powder becoming nearly white on reprecipitation by alcohol from aqueous solution. From 5.1 to 7.9 per cent. was obtained from 4 chestnut woods, the lowest from a light colored wood I, yielding the best liquors for clearing; the highest yield was from the red Corsican wood. The alkaline extracts of the woods II, III, IV were strongly yellow and that of wood I colorless, showing that the dye-stuff was not bound to the tannin, else it had been removed by the ammonia.

W. J. K.

Tanners' Institute. Report of Third Year. The pamphlet of 56 pages published by Pratt Institute with the above title embraces the Director's Report, Report of Investigations by Dr. Allen Rogers, Students' Investigations and Prospectus of Courses. The Director, Samuel S. Edmonds, reports that the sum contributed by the National Association of Tanners, upwards of $5,000 yearly, has been expended for scholarships, observation trips, special lectures by experts, and upon investigations. Twenty-one students were enrolled in 1913-14, seven of these taking the course in Applied Leather Chemistry, which is a post-graduate course. An exhibit was made at the Boston Shoe and Leather Fair. Two prizes were awarded in the tanning courses and one in the course in applied leather chemistry. Besides visits to nearby tanneries, the students made an extended tour of the middle west. A similar tour is in anticipation for the current year.

The value of the permutit process (see JOURNAL, Vol. 7, pp. 423-9, and Vol. 9, pp. 143-58) in softening leach-house waters was tested. A water having a total hardness of 40 parts per 100,000 was used to leach various materials, the temperature being kept below 70° C. The liquor so obtained was made into extract and the extract analyzed. The same operations were conducted with water from the same source which had been treated

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by the permutit process. Results are given in the table, figures are percentages.

Materials	Water	Total solids	Soluble solids	Insolubles	Non-tannins	Tannins
Myrobalans	treated	58.3	54.9	3.4	19.2	35.7
	untreated	60.0	54.3	5.7	20.0	34.3
Guara	treated	76.2	67.5	8.7	21.4	46.1
	untreated	76.5	67.2	9.3	22.2	45.0
Sumac	treated	44.5	43.8	0.7	16.0	27.8
	untreated	44.0	42.9	1.1	17.5	25.4
Mangrove	treated	57.1	54.9	2.2	15.9	39.0
	untreated	56.7	53.0	3.7	15.2	37.8
Hemlock 1	treated	25.1	20.9	4.2	8.0	12.9
	untreated	24.9	20.4	4.5	8.1	12.3
Hemlock 2	treated	52.2	51.7	0.5	26.5	25.2
	untreated	52.2	48.6	3.6	24.0	24.6
Quebracho	treated	34.0	30.2	3.8	6.8	23.4
	untreated	34.1	29.1	5.0	7.2	21.9
Chestnut	treated	51.4	50.8	0.6	31.2	19.6
	untreated	50.8	49.1	1.7	32.0	17.1
Treated quebracho.....	treated	88.9	88.4	0.5	25.1	63.3
	untreated	88.4	87.4	1.0	28.8	58.6

(In eight instances the tannins and insolubles as given in the table were not equal to the difference between solubles and non-tans or totals and solubles respectively. We have assumed that the direct values are correct and have changed those found by subtraction.)

Experiments have been tried in the use of ozone for bleaching hair, but without result. A number of experiments have been made with Neradol D. An abstract of this will appear in the JOURNAL later. Tests were made of guara with a view to its suitability as a substitute for sumac. In the report of these the opinion is expressed that guara is a mixture of valonia and algarobilla. The results of guara tannage are regarded as satisfactory.

Abstracts of the students' investigations will be published later.

The Theory of Leather Formation. W. FAHRION. *Collegium*, 1914, pp. 707-10. This is a reply to Powarnin (abstract, ante, pp. 567-70) whose criticisms are rejected mainly on the ground that he does not know the author's publications. The latter abandoned (1909) his earlier theory of salt formation in leather and essentially limited the assumption of oxidation in the hide fiber. Verbatim: "The chemical part of tannage consists

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of the formation of a complex through condensation processes." This includes or fits Powarnin's new theory as well. Beginning with chamoisage, it was shown that unsaturated fatty acids of fish oils yielded peroxides which were the real tanning agents. It was concluded that active oxygen in both fat and quinone tannage reacts with a nitrogenous group of the hide molecule. Bamberger having shown that active oxygen may react with either primary, secondary or tertiary amines, the author left the question open which nitrogenous groups of the hide are in question and had used the primary group solely for illustration. Powarnin criticizes the author's formula of di-anilidoquinone and overlooks that it was later substituted by that of diphenylquinonedioxime, $C_6H_4\begin{matrix}N.C_6H_5.OH\\N.C_6H_5.OH\end{matrix}$.

Powarnin employs Engler's peroxide formula in his chamoisage reactions, but Staudinger has convincingly shown that it must contain the unsymmetrical group, $\begin{matrix}R_1 - CH\\R_2 - CH\end{matrix}\!\!>O = O$.

The author found that *o*- and *p*-diphenols and oak tannins formed active oxygen by action of water and applied the observation to the tannage process. Powarnin objects to the slight amount of peroxide formed, but small amounts add together, if they react with the hide when generated.

W. J. K.

The Determination of Free Sulphuric Acid in Leather. J. PAESSLER. *Collegium*, 1914, pp. 567-92. In a previous publication (see p. 244, May JOURNAL), Dr. Paessler has stated that the more free sulphuric acid is offered to white hide, the smaller the proportion of that acid which will be absorbed by the hide, and the smaller the quantity offered, the larger will be the proportion absorbed. In like manner, the larger the percentage of free acid in hide in contact with water, the larger will be the proportion of that acid given up to the water, and the smaller the acid content of the hide, the smaller the percentage of the acid which will be given up to the water. These points are illustrated by a number of experiments in which pieces of white hide of approximately equal weight (7 grams) are exposed to the action of dilute acid, and afterward immersed in distilled water. Pieces immersed in 100 cc. each of N/10 sulphuric acid for 12, 24, 48, and 72 hours took up the following amounts of acid per 100 parts hide, respectively, 1.88, 1.88, 1.97, 1.77. In a similar experiment with N/20 acid the amounts taken up were 1.33, 1.50, 1.49, 1.52. Similarly with N/50 acid, 1.12, 1.14, 1.13 and 1.16. The author concludes that a 24-hour period is sufficient. In another experiment pieces of hide were placed in varying quantities of water, the quantity of acid in each case being the same; 10 cc. of N/5 acid. With dilutions of 1:5, 1:10, 1:15 and 1:20, the amounts of acid absorbed by 100 parts hide were 1.17, 1.14, 0.92 and 0.78. Pieces weighing about 45 grams were placed in 200 cc. of N/20 and N/40 acid, taking up 1.05 and 0.053 per cent. respectively. The converse process

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was carried out with the 7-gram pieces, placing them each in a section of glass tubing with parchment paper tied over one end, filling the tube with water and suspending in a vessel of water. The quantity of acid diffusing out into the water in the outer vessel was tested at the end of 12-hour periods up to 120 hours, after which no increase was observed. A table shows total amounts of acid dialyzed out. From pieces containing at the start acid equivalent to 13.35 and 12.1 cc. N/5 acid, the respective amounts found were 4.25 and 4.4 respectively. Less acid pieces in general give lower results down to those which had 3.8 cc. and gave up 0.35 cc. N/5 acid. The quantities of acid found in the dialysate are not proportional to the amounts in the hide.

Under the title "The Sorption Theory, a Theory of the Dyeing Process," G. von Georgievicz, published in *Chemiker Zeitung*, 1914, No. 42, p. 445, a résumé of former articles in *Monatshefte Chem.*, 1911, pp. 655 and 1075, 1912, p. 45, and 1913, pp. 733 and 751. He shows that for wool, laws similar to those governing hide hold good. If C_1 and C_2 represent the concentration of acid in the hide and in the dialysate respectively, then the xth root of their quotient is a constant; $\sqrt[x]{\frac{C_1}{C_2}} = K$. Dr. Paessler proceeds to work out values for x and K from the results of his experiments. He concludes that three processes go on in the taking up of acid by hide, first simple absorption or soaking up, second "adsorption," and third chemical reaction. The first takes place almost exclusively when the solution is very dilute, and is proportional to the acid strength, corresponding to a value of 1 for x in the formula. As the acid strength increases, the proportion of adsorption (formation of "solid solution") increases, and after a time with further increase of acid strength, chemical reaction begins. The effect of the first action is represented by a slanting line (proportionality shown by straightness). The effect of adsorption is represented by a curved line, amounts adsorbed increasing disproportionately as the acid strength rises. The effect of chemical union is represented by a horizontal line. If all three actions be represented by a single line, we have the "sorption curve" which is the sum, graphically speaking, of the other three.

A series of experiments similar to those tried with pieces of white hide was carried out with pieces of leather. Six pieces, weighing 5 grams each, were each placed in 250 cc. of water, the quantities of acid in the water ranging from 0.0049 to 0.049 gram. The percentage of this acid, taken up by the leather ranged from 47.5 to 25. The pieces were then placed in 200 cc. of water each for 24 hours, and the amount of acid diffusing out was estimated by titration. The quantities of acid in the pieces of leather ranged from 0.00465 to 0.0196 gram. The amounts found in the water at the end of 24 hours ranged from 0.00147 to 0.00698 gram, the percentages of acid lost by the leather, however, being nearly constant. Of the acid present in the leather at the start, the percentages lost were as follows, beginning with the piece having least acid: 31.6, 29.2, 29.4, 28.9,

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29.5, 30.6, 35.6. The method serves to indicate qualitatively the presence or absence of sulphuric acid in the leather quite sharply. (This qualitative method was described and illustrated by J. S. Rogers at Chicago. See JOURNAL for Dec., 1914, pp. 503 and 505.) The change of color on the part of the Congo red indicator may be due to any free acid, and it takes place more quickly the greater the proportion of free acid present. If the indicator turns in 3 or 4 hours, any one of the following acids may be present: sulphuric, hydrochloric, oxalic, formic, acetic, lactic. The first two are harmful. Whether or not oxalic is so is not certainly known. For the others, any quantity likely to be present is not harmful. To test for sulphuric acid, warm the finely cut leather with dilute HCl, to bring into solution free sulphuric acid or its soluble salts. To the filtered solution add barium chloride. If there is no precipitate there is no free sulphuric acid. A white precipitate shows either free or combined sulphuric acid, and further examination is necessary to determine which. For the dialysis test, Dr. Paessler recommends a parchment paper thimble made by Schleicher and Schüll.

The quantitative estimation of the free acid is carried out as follows: Two pieces of the leather in question are weighed out, one twice as heavy as the other. Each of these is placed in the same quantity of water (200-300 cc.), and frequently agitated for 6 hours. They are then taken out, rinsed, and the acid diffused into the water estimated by titration with N/10 barium hydroxide solution, using a rather large quantity of methyl-orange-indigo solution as indicator. Assuming that the value of x in the Georgievicz equation is 1, because of the low concentration of acid, the quantity of acid in the leather may now be calculated by means of a proportion. A piece of leather containing 0.73 per cent. of free sulphuric acid (how determined is not stated) was subjected to this process and the result figured out to 0.65 per cent.

In this work the dialyzing apparatus was not used, in order that all the free acid which had gone into solution might be estimated. By the use of methyl-orange-indigo solution as indicator the neutralization point can be determined definitely enough. The author states that a research is in progress in which it is hoped to get results with the dialyzed solution, thus avoiding the interference caused by the presence of tannin.

If it should be found that the percentage of sulphuric acid is 1 per cent. or over, it may be necessary to use smaller pieces or larger quantities of water so as not to pass the limit of concentration for which x in Georgievicz formula may be taken $= 1$. Unless it is known that no other free acid is present, the sulphuric acid in the solution must also be gravimetrically estimated by the usual method. If this latter result is lower than that found by titration, some other acid is also present.

The process fails if both organic acids and salts of sulphuric acid are present in addition to free sulphuric acid, or where a leather contains aluminum sulphate. In the first case, titration with barium hydroxide forms soluble barium salts with the organic acid, and these are transposed

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by the soluble sulphates, releasing additional acid and so giving too high a result.

Additional on the Determination of Pentoses in Tanning Extracts. J. L. VAN GIJN and H. VAN DER WAERDEN. *Collegium*, 1914, pp. 711-4. The criticisms of Moeller in *Collegium* No. 532 and Reed and Schubert (ante, p. 131) have caused the authors to return to this subject.

They could not confirm the American authors that an extract of quebracho wood in cold water gives the same reaction as mangrove extract, but on the contrary find it gives the characteristic quebracho reaction; after addition of the phloroglucin-HCl mixture, the solution becomes first yellow, then green, with gradual formation of a slight black precipitate. No quebracho extracts examined yielded methyl furfurol. Mangrove extracts always gave a color change from yellow to red-brown with formation of a brown precipitate, practically soluble in warm alcohol. Rhamnose was subjected to this test. In the distillate the color remained a little brighter and the precipitate was brick red. The authors believe that always in the case of mangrove very small quantities of furfurol pass over in distillation and influence the color. The observation of Reed and Schubert in regard to the decomposition of rhamnose by heating 4 hours at 4 atmospheres, the authors could only partially confirm. After this treatment, 200 mg. of rhamnose yielded 119 mg. of phloroglucid instead of 125 mg. obtained by the ordinary distillation.

Reed and Schubert also state that by extraction under pressure methyl-pentoses are transformed into pentoses. To test this statement a series of extractions of mangrove bark was made under varying conditions, and also the effect of addition of organic acids was tried. Contrary to Moeller, these had no effect, and no trace of furfurol could be detected with phloroglucin. Only with pressure extraction at 2-3 atmospheres could an increase of pentoses be proved. Extraction at 4 atmospheres would be in practice exceptional. Moeller declares that vacuum evaporation would expel all the furfurol and methyl-furfurol from any extract. The authors, however, could not find methyl-furfurol in distillates from the evaporation of mangrove extracts. They also find that the original substances yielding furfurol remain in the bark after extraction. Five grams of mangrove bark were distilled with 12 per cent. HCl, and the residual bark and extract from a like amount, subjected to a parallel test.

		Mgs. phloroglucid of	
	cc. distillate	furfurol	methyl-furfurol
Original bark	100	47	18.0
Spent bark	100	78	5.5
Extract	250	0	97.0

Mallet extract also yields methyl-furfurol, but its substitution for mangrove is doubtful because of price. W. J. K.

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ACTIVE.

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ASSOCIATE.

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exchange unbound numbers for bound volumes will please send them prepaid to the editor at Ridgway, Pa. Missing numbers will be supplied at 25 cents each. Copies of previous volumes may also be obtained on the same terms.

VOTE ON CHANGES IN METHODS.

No. 1.—Discontinue "Provisional Method for Color Valuation of Tanning Materials," as described at top of page 28, in the 1914 booklet.

No. 2.—Discontinue "Provisional Methods for the Analysis of Oils and Fats," as described on pages 30 to 38, inclusive, in the 1914 booklet.

No. 3.—Addition to Methods, regarding test for presence of Sulphite-Cellulose, as described on pages 130 and 131 of the March, 1914, JOURNAL.

No. 4.—Changes in Methods, "Official Methods for Sampling Tanning Materials," as described on pages 492 to 496, inclusive, of December, 1913, JOURNAL, (with the exception that under the heading [I] "Solid, Powdered and Pasty Extracts," only "Proposal [A]" is submitted, by action of the Council).

New York, Jan. 12th, 1915.

MR. W. K. ALSOP, *Editor,*
Ridgway, Penna.

Dear Sir:

Following is the vote on the various changes and additions to the official methods:

Proposition No. 1.—26 votes cast, 24 "yes," 2 "no"—Carried.

Proposition No. 2.—26 votes cast, 21 "yes," 5 "no"—Carried.

Proposition No. 3.—26 votes cast, 22 "yes," 4 "no"—Carried.

Proposition No. 4.—24 votes cast, 16 "yes," 8 "no"—Carried.

Yours very truly,

H. C. REED, *Secretary.*

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NOTES FROM TANNING COURSES, TANNERS' INSTITUTE.

The courses in Tanning and Applied Leather Chemistry conducted at Pratt Institute have enrolled a full class in each of the courses. Eighteen men are now in attendance in the tanning course, and four in the course in applied leather chemistry. The scholarships provided annually through the generosity of the National Association of Tanners for the support of young men who would otherwise be unable to attend the tanning courses were again offered to this year's classes. The payment of the first installment of this year's scholarships has recently been made.

ANALYSIS OF LACTIC ACID.

By T. A. Faust.

In view of the fact that the A. L. C. A. has no official methods for the analysis of lactic acid, there have been some differences as to the methods to be used by the chemists of the purchaser and of the manufacturer. Recently, Mr. Carnell of Harrison Bros. and the writer met and discussed thoroughly the various methods; and later three samples were analyzed, each chemist using his own methods. The result of this laboratory work may be of some interest, and is herewith presented as a suggestion for the Committee on the subject, of which Dr. Balderston is Chairman.

The methods used by Mr. Carnell are as follows:

Weigh off about 10 grams of sample (of dark lactic acid take half as much), make up to 250 cc. in a graduated flask, take out 50 cc. and titrate to neutral point with N/5 caustic potash (phenol-phthalein)—*1st Titration.*

Let A stand for number cc. alkali used; multiply A by 0.3, add that much alkali in excess, heat on water bath for 15 minutes, cool, titrate back to neutral point with N/5 acid—*2nd Titration.*

Let B stand for actual number cc. alkali used (after deducting the N/5 acid).

Take another 50 cc. and evaporate in a platinum dish on water bath three times down to half volume, cool, making up to 50 cc. again, add same amount of N/5 alkali, including the excess as

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used in 2nd Titration, heat on water bath 15 minutes, cool, titrate back to neutral point with N/5 acid—*3rd Titration.*

Let C stand for actual number cc. alkali used (after deducting the N/5 acid).

Calculation:

B — A = cc. to be calculated to Lactic Anhydride.

B — C = cc. to be calculated to Acetic Acid (volatile).

C — (B — A) = cc. to be calculated to Lactic Acid.

The methods used by the writer are as follows:

Ten grams of the sample are dissolved in cold distilled water, and the volume made up to 1 liter.

One hundred cc. of the above solution are titrated with N/10 caustic soda, using phenol-phthalein as indicator to a faint pink, which remains permanent for 1 minute.

An excess of 20 cc. N/10 caustic soda is then added to the above solution, placed in a boiling water bath for 10 minutes, cooled and titrated back with N/10 hydrochloric acid, using phenol-phthalein as indicator.

The number of cc. used in the first titration represents the total free acid.

The number of cc. used in the second titration, subtracted from 20, represents the anhydride.

Volatile Acid.—Two hundred cc. of the diluted acid is placed in a round bottom flask, connected with a spiral condenser by a tube inserted in a rubber stopper which tightly fits the mouth of the flask; the tube is bent upwards and leads into a trap, to prevent any mechanical loss, and above the trap is bent at an acute angle to lead into the condenser, the outlet of which dips below the surface of distilled water placed in the receiving flask.

Distillation is carried on until about 20 cc. remains in the boiling flask; the distillate is titrated with N/10 caustic soda, using phenol-phthalein as indicator to a permanent pink. The number of cc. required represents the volatile acid and is calculated to acetic.

The number of cc. of alkali required for this last titration is deducted from the number of cc. required for an aliquot part in the first titration, and the remainder is called the free lactic acid.

It will be noticed that excepting volatile acids, there is very

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little difference in the methods between the two laboratories. The table published herewith shows the results of the analyses of the three samples by the two collaborators, using the two methods; A being the methods used by the writer, and B the methods used by Mr. Carnell. The available lactic acid as reported by A is rather lower than as reported by B. This is principally due to the difference in volatile acids. The total acid as lactic reported by A agrees very closely with the available lactic acid reported by B; the volatile acid should, however, be deducted from B's figures, which will make the agreement exceedingly close. It is therefore evident that the methods for free lactic acid and anhydride are of sufficient accuracy, but a method for volatile acid should be devised.

Following the collaborating work noted above, the writer carried on some investigations to obtain additional information relative to the subject. Dr. Philip wrote an article, published in the A. L. C. A. JOURNAL, 1906, page 189, in which he states that lactic acid forms anhydride on standing in the cold. To determine this, the writer titrated the free acid on a number of samples which had been standing in the laboratory for from 3 to 6 months, and in no case was any great difference noted. Dr. Philip furthermore states that anhydride, when used to delime, forms unstable salts which break up into lactic acid, but this point is rather doubtful.

A committee of the A. L. C. A., appointed in 1906, proposed a method for determining volatile acids, which consisted of distilling the acid twice, combining the distillates, adding a 1 per cent. permanganate solution, again distilling, and titrating the distillate. The idea of the addition of permanganate was to destroy any lactic acid which may have been mechanically carried over. The report of the committee, however, was not in favor of this suggestion. The evaporation method (that is the method of evaporating on a water bath a solution of the lactic acid three times), was tried by this same committee, but gave considerably higher results than the distillation method, although more concordant results.

Mr. McLauchlan investigated this subject very thoroughly in 1907, and he found that lactic acid volatilizes on heating in dilute

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solutions; but it was later shown by Mr. Claflin that the evaporation method does not remove the acetic acid.

The following year Mr. Small was appointed Chairman of the committee, and he found the evaporation method unreliable, proving that the acetic acid was not removed by this procedure. He also found that adding permanganate to the combined distillates in the above-mentioned distillation method, was not satisfactory; and that formic acid, if present, would be destroyed by the permanganate. He proposed the following method: To distil 100 cc. of the dilute solution to 5 or 10 cc., make up the residue to 100 cc. and again distil to 5 or 10 cc., combine the distillates, make up to 200 cc. distil the combined distillates and titrate the final distillate.

The writer has found the method given above, of determining the volatile acids by distilling only once, to give fair results. The comparison of the results obtained by this method and by the evaporation method, as shown in the table, shows fairly concordant results as far as the commercial acids are concerned, but does not show concordant results on the C. P. acid. Chemically pure acids may contain propionic acid, which might account for this difference.

However, a comparison of the results obtained by the writer, and those obtained by Mr. Carnell, by the evaporation method, shows that they do not agree at all.

A sample of commercial acid showing about 1 per cent. of volatile acids, had added to it 4 per cent. of acetic acid and distilled once. The distillate showed 4.11 per cent. acetic acid, so that not quite all of the volatile acid was recovered. On the other hand, another sample of acid had added to it sufficient acetic acid so that the sample contained 50 per cent. acetic acid. Distilling only once, this showed 36.90 per cent. of volatile acid. It is therefore evident that where only a small quantity of acetic acid is present, the single distillation method will show at least 90 per cent. of the volatile acid; but where a large quantity of acetic acid is added, it is necessary to make more than one distillation, and it is believed that the method as submitted by Small (see above), should be used for such an acid.

The writer does not believe that it is necessary to have an

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absolutely accurate method for this determination, and where only 1 or 2 per cent. of volatile acid is found, it is inconsequential, in that this volatile acid has some neutralizing and plumping powers, and such a percentage does not indicate any wilful adulteration. Furthermore, where only a small quantity is present, the single distillation method which requires only a short time for operation, will give practically all the volatile acid and will minimize the mechanical loss of lactic acid, and is of sufficient accuracy for commercial purposes.

Where, however, titration of the first distillate shows a very large quantity of volatile acid present, it is probably necessary to redistil the residue in the flask, titrate the second distillate, and combine the readings.

The latter sample, that is the sample containing 50 per cent. acetic acid, was also analyzed using the evaporation method, and here only 34.64 per cent. of volatile acid was found, which is even lower than that found by single distillation. It is, therefore, evident that the distillation method is the more reliable, although probably the method as proposed by Small should be used where more than say 3 per cent. of volatile acid is found on titrating the first distillate. This, however, is very unusual.

The writer would make the suggestion that in acids showing a low quantity of volatile acids and indicating no adulteration, the titration reading to phenol-phthalein be reported, Total acid as Lactic, for this is the percentage which really indicates the strength of the acid.

Regarding the matter of anhydride, there has been some work done abroad recently regarding its value; the general consensus of opinion of the chemists abroad being that the anhydride has no value in the tannery.

The writer believes that where lactic acid is used for plumping purposes in tannery liquors, the solutions always being acid, the anhydride does not have any value; but that in the beam house where lactic acid is used for deliming, where the hides are alkaline, this lactic anhydride does have neutralizing power. This is borne out somewhat by the method of analysis, in which an excess of alkali is added to the solution, when the anhydride combines with the excess alkali.

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The only objection to this is the fact that this determination is carried on in the hot solution, and while theoretically correct, does not indicate conditions in the beam house. Perhaps if the determination of the anhydride was made in the cold, the percentage of anhydride reported would indicate to what extent the anhydride is of value in a bate which will become alkaline before the hides are taken out.

A determination of the anhydride in lactic acid was made by adding an excess of alkali and allowing to stand in the cold for 15 minutes (this being comparable to beam house conditions), and there was found present 4.80 per cent., although by making the determination in the regular way in the hot, 7.20 per cent. was found.

It is hoped that this year's Committee will do some additional work on this latter question.

The following method of reporting lactic acids is suggested:

Free lactic acid.
Lactic anhydride.
Total lactic acid and anhydride.
Volatile acid calculated as acetic.
Total acid as lactic.

The writer is indebted to Mr. Kernahan for his assistance in the laboratory and experimental work conducted in the preparation of this article.

	Special light		Regular light		Chem. pure	
	A	B	A	B	A	B
Available lactic acid	37.08%	38.94	34.87%	36.82	69.35%	71.84
Lactic anhydride	5.60	4.41	5.36	5.29	16.32	17.43
Lactic acid and anhydride..	42.68		40.23		85.67	
Volatile acid	1.32	None	1.53	0.13	2.13	0.54
	1.92[1]		1.38[1]		0.48[1]	
Total acid as lactic.....	39.06		37.17		72.54	
Total strength		43.35		42.32		90.10

NOTE ON EPSOM SALTS.

By W. K. Alsop.

(The following experimental results were presented as a supplement to the report on standard methods of reporting results

[1] Using Carnell Method.

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of analyses read at the Chicago meeting, Oct. 28, 1914. The report was printed in the November number of the JOURNAL, 1914, pp. 479–84.)

Portions of a thoroughly mixed sample of leather containing Epsom salts were ashed at different temperatures, with results as follows:

No. 1. Bright red heat (Meker burner)—Ash, 1.95 per cent.; SO_3 in ash, 0.49 per cent.

No. 2. Red heat (Bunsen burner)—Ash, 2.25 per cent.; SO_3 in ash, 0.78 per cent.

No. 3. Heat just sufficient to burn—Ash, 2.37 per cent.; SO_3 in ash, 0.85 per cent.

The magnesium in the ash was determined and figured to Epsom salts, giving 2.27 per cent. $MgSO_4$ equivalent to 4.65 per cent. crystallized Epsom salts.

In order to determine the quantity of water lost by Epsom salts in drying, a sample of pure salts was used, giving the following analysis: $MgSO_4$, 52.45 per cent., Water, 47.55 per cent. About 3 grams was dried in hot air oven at about 105° C.

No. 1.—Dried 2 hours, loss 37.72 per cent., or 79.12 per cent. of the water present at the start.

No. 2.—Dried 4 hours, loss 38.90 per cent., or 81.80 per cent. of the water present at the start.

No. 3.—Dried 6 hours, loss 39.14 per cent., or 82.31 per cent. of the water present at the start.

Water not driven off, 8.41 per cent. After 6 hours' drying, the magnesium sulphate contains approximately 1 molecule of water. (1.07 mol.)

If leather contains 5 per cent. salts, this indicates about 0.50 per cent. moisture held by the $MgSO_4$ after drying at 105° C. Probably, however, this does not interfere in the combined tannin figure to any extent, as the salts are washed out in the water soluble, and thus the water held, while not shown in the water as determined, will probably be reported in the water solubles, the errors thus counterbalancing each other.

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HYDROGENATION OF OILS.*

By Victor G. Lumbard.

MR. ALSOP: Mr. Lumbard has a paper on "The Hydrogenation of Oils," and I would be glad if he would present it to us.

MR. LUMBARD: Mr. President, I would ask Dr. Rogers to read my paper, because it may be of interest to the American Leather Chemists Association. I returned from Germany a short while ago, being forced out of that country rather hurriedly because of the situation that exists there now, but while there I was in many chemical laboratories, and had an opportunity to observe the hydrogenation process. While the industry is still in its infancy, the American Leather chemists may soon have an opportunity to investigate these products, and if so this paper may give you a little preliminary knowledge of what the process is. I have translated this as I got it from my German friends. It is very short, and I have had the copy digested, and have just turned it over to Dr. Rogers, and if he will do me the honor to read it I will appreciate it.

Dr. Rogers read Mr. Lumbard's paper, which follows:

It is everywhere known that those industries which work up fats, have been seriously upset for many years by the considerable advance of prices of raw materials. The rapid development in the manufacture of fats for nourishment, especially has made solid fats so scarce and expensive that the soap industry which absolutely requires solid fats for the manufacture of solid toilet and household soap, have found it very difficult to get the necessary raw materials. As there are still large quantities of liquid fats obtainable at quite low prices, it has consequently become a necessity to find a chemical method for the transformation of the liquid raw materials into solid ones. The problem has been solved by the catalytic method of hardening fats.

The liquid fats differ from the solid ones by the low percentage of hydrogen of their fatty acids, by the unsaturated character which besides the liquid condition involves still other properties, by the tendency to rapid oxidation in open air, by the dark coloring and by the disagreeable fish-odor of the highly unsaturated

* Eleventh Annual Meeting of the A. L. C. A., Chicago, October 30, 1914.

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fish oil fatty acids which hampers the possibility of employing fish oils.

For more than 50 years the problem of hardening fats occupied chemists and manufacturers, but none of the many processes which have been suggested could be carried out in practice.

With the development of physical chemistry, the science of the "katalysatoren" has got footing, and after it had been shown by the experiments of the French savants Sabatier and Senderens, that by the aid of nickel in a fine state of subdivision it is possible to join hydrogen to unsaturated compounds, W. Normann found that unsaturated fats or fatty acids, in which finely divided nickel was suspended, could be made to unite with hydrogen. In Germany the process of Normann for a long time did not attract any attention, but it was taken up by the English firm of J. Crosfield & Sons, and perfected in a few years to an important technical process which supplied in 1906 many tons a day.

The German patent passed on to the Naamlooze Venootschap Anton Jurgens, who established in 1911 the Germania Oelwerke, where to-day 100 tons of liquid fat, mostly fish oil, are being hardened every day.

A great number of patents have been asked for the employment of the nickel method, which, however, in Germany are all dependent on the Normann patent. The most known of these processes is the one of Wilbuschewitsch. After an arrangement with the Germania Oelwerke they now use their process for the manufacturing of hardened oils for food purposes.

Besides the nickel method, another one developed from the experiments of Paal, which used palladium as a catalyzer. The addition of hydrogen in this case is done more quickly and at a lower temperature, and the products are very satisfactory, but in view of the high price of palladium competition with the nickel method is impossible.

Great attention has been called to a process of Erdmann and Bedford, in which oxide of nickel is substituted for nickel. The oxide of nickel seems to be more insensible towards the soilings of the oil and the hydrogen than the metal in fine distribution. This process has been also perfected in England. A factory in

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Germany, the Oelwerke Hydrogen, will start manufacturing within a short time. A heated dispute which is not yet decided, is carried on about the question whether in the Erdmann process also, nickel is the effective catalyzer, as is supposed by Normann, or whether the conception of Erdmann is right, who says that the oxide of nickel is being reduced to suboxide, which acts as a catalyzer. A German patent for the nickel oxide method has just been granted, after the English patent has been in force for several years.

A number of other processes are based upon nickel compounds, which during the treatment with hydrogen are transformed to nickel. The method of Wimmer-Higgins, for the exploitation of which the Fettraffinerie A. G. at Brake has put up a factory, is using especially formate of nickel. This method is also closely connected with the one of Normann.

The hardened fats, hardened fish oils, linseed oil and cotton-seed oil are to-day used to a very large extent for soap manufacturing, on account of the superior foaming properties, in conjunction with other fats.

For the manufacturing of edible fats, the hardening of fats is of utmost importance, because by the aid of this method it is possible to use vegetable oils in place of animal fats, after the former have been hardened to the proper melting point.

Manufacturers, however, on principle, do not use hardened fish oil for food products, in order not to give the producers of natural butter any more topic to agitate against margarine, although the production of butter in Germany is not sufficient by far to cover requirements.

DISCUSSION.

DR. ROGERS: I might say that one man in this country has done a great deal on this question, and that is Carleton Ellis, who has taken out several patents. And down on Staten Island, Procter and Gamble are manufacturing hydrogenated oils on quite a large scale. The fact of this manufacture is kept rather quiet, because there are some basic patents, and they do not want the thing to come to an issue. They are making a substitute from cocoanut oil. I had several pounds of it given to me

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to take home to my wife, and she made some pies with it and cooked some cakes in it that were pretty good. I had a sample a while ago of hydrogenated whale oil that was being offered to the trade in place of stearine, that looked pretty good. "Crisco," I think, is a hydrogenated cottonseed oil; it is made by Procter and Gamble.

MR. LUMBARD: The reason I wanted to call the Leather Chemists Association's attention to that little article I brought over from Germany was, that in my trip to Germany I visited many tanneries, and saw these products in actual use, especially solidified linseed oil, of which they used a good deal in dressing patent leather. They were also using a lot of solidified cottonseed oil. The war has no doubt stopped exportation of that oil. I saw it being used for replacing the old fashioned saponified linseed oil, which they used as a top dressing in their patent leather, and especially in their vegetable tan patent leather. And they have practically replaced the raw linseed oil they previously used with this solidified linseed oil.

MR. COX: We have carried on some experiments with a hydrogenated linseed oil which we got from England. It can be used as a fat-liquor, we think, up to 9 per cent., and still japan can be put on top of it without de-greasing it, and the japan not loosen.

MR. YOCUM: Did I understand Mr. Cox to say that in using the hydrogenated oil you could use 9 per cent. of the weight of the leather, and still japan?

MR. COX: Yes, you can take these, after they are solidified by the hydrogenation process, and sulphonate them, and they will still be solid after sulphonating, and the melting point will run very high. That is being worked out now to use in non-degreased leather. Leather will carry 9 per cent. of the oil, and show no objectionable grease at all.

MR. FAUST: I would like to ask Mr. Lumbard whether he went to any harness leather tanneries, and whether hydrogenated whale oil is being used as a stearine substitute in that country?

MR. LUMBARD: It is not being used exactly as a stearine substitute, but it is used to replace many of the oils such as moellons. I found that in conjunction with stearines and tallow

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that it has better carrying qualities, absorbing and carrying the greases in better, so the tanners told me, and it leaves the flesh very clean. It has been adopted for dressing, for instance, on satchel, bag and case leathers, because in dressing with it it does not run. It is about of the consistency of a very heavy butter, and when it is subjected to heat becomes limpid. They will then mix it with a little sulphonated oil, to make it flow, and when they hang the leather on the hooks they claim that it does not drip and that the absorption of the oil is clean and clear, and it doesn't run to the skirts as so many of those free running oils do. So on all those harder leathers it has been used to a great extent, and also on harness leather.

MR. COX: With this oil it is possible to make an emulsion and take sole leather of very light color, and dip the leather into it, and have the leather dry out without any loss in color.

MR. SAXE: Mr. Lumbard, which oil did you prefer for the patent leather, was it fish oil or vegetable oil?

MR. LUMBARD: Fish oil and linseed oil, because cottonseed oil seems to harden more than the other oils.

MR. SAXE: Did you give preference to either of the hydrogenated oils, whether it was the fish or cottonseed?

MR. LUMBARD: They give preference to the fish oil.

MR. YOCUM: Mr. Lumbard, would it be possible to sulphonate the oil and then harden it so as to bring it up to that condition?

MR. LUMBARD: In Germany they blend hardened oil with sulphonated oil to carry it into an emulsion, and they use it in that form in fat liquor.

MR. COX: To answer that question, it is perfectly possible to take one part of the sulphonated hydrogenated product, and to combine it with four parts of a fat such as stearine, melted, and have it form an emulsion, and put the leather in it, and hang it up while it is still wet, and it will come out without any discoloration.

MR. LUMBARD: What interested most of the German tanners in this product, is the fact that when combined with the sulphonated oil, the linseed oil being a very drying oil, will carry into the leather, and it leaves the surface absolutely clean and free from any fats that may come up during the process of baking in

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the ovens. Ordinarily unless the leather is degreased, the first coat has a tendency to peel. They do not experience any of those difficulties in the use of this hardened linseed oil.

MR. YOCUM: Mr. Lumbard, does the hydrogenated linseed oil still have its drying property, or can it be boiled into a sweetmeat or into a varnish?

MR. LUMBARD: I asked, regarding that, and they said they do not use it for boiling varnish. When this oil is blended with a sulphonated fish oil, which they use considerably in conjunction with it, it seems to lose considerable of the oxidizing effect, that the original linseed oil would have. It leaves the surface very clean. The oil does not flow out, it does not come out in the heat of the ovens, especially under a temperature of 140°, to which they subject leather in their ovens.

MR. YOCUM: But does it dry after it is hydrogenated?

MR. LUMBARD: They follow up the primary coat with a collodion coat, and it is said that the collodion coat adheres to the sweetmeat coat better where they use the solidified oil than where they use the free oil in fat-liquoring.

MR. YOCUM: As a matter of practice, can you after hydrogenating linseed oil then boil into sweetmeats or a daub?

MR. LUMBARD: I couldn't tell you that. I asked a tanner about it and he said that they intended to carry out some further research work in that line. Are there any of the gentlemen assembled here, of the leather chemists, who are in any way connected with patent leather works? If there are, it probably would interest you to hear what I saw in Europe.

(A visitor announced that he had some connection with patent leather works.)

When I was over in Germany I was very much interested in the new "sun process," the artificial sun—of course you have heard of that. In Germany there are places where the atmospheric changes are so sudden that in a few minutes a cloud may come over the sky and a rain storm may come at once. They will immediately ring a bell, and they have a system in their factory like a fire patrol, everybody runs for a side of patent leather and immediately gets it under cover so it will not become spattered by the rain and in that way stained. They use the

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Cooper-Hewitt light, from which they filter out the ultra-violet rays. They put these lamps in the ovens. I saw one oven that had 3,500 lights in it. The lights were suspended along the wall, and the light is so intense that the men who take care of the ovens wear hoods and extra dark goggles to protect their eyes from the rays. The leather passes on a frame on an endless-chain-like conveyor. The ovens are approximately about 150 feet long, and are built in three tiers, one tier above the other. The frames are suspended on chains, and pass in front of the lights. You can imagine what intensity of light there is with all those lamps on one wall. It takes the leather about an hour and a half to pass the lights, and the action of the rays on the japanned leather is such that when it comes out at the other end and is allowed to cool you can take your finger and use the ordinary snapping test, and there is absolutely no tackiness, and no "stick." I saw some leather that had been laid away grain to grain, for six months without a particle of adhesion between the japanned surfaces. Now there is not an oven of that character in the United States, and yet they have adopted our invention, and are using it in this way.

MR. SAXE: Don't you know that an attempt to make leather under those conditions was made in Buffalo a few years ago?

MR. LUMBARD: Yes, I know that, but it was not under the same auspices, and they did not use that light, nor did they filter out the ultra violet rays.

Now as to the Cooper-Hewitt light—Dr. Rogers probably knows as much about that light as I do,—they filter out the ultra-violet rays and get an entirely different action. They claim that they get the same action that the sun has as to drying effect.

MR. SAXE: Do you think the Germans took that from us, Mr. Lumbard?

MR. LUMBARD: Yes, I know they did.

MR. YOCUM: Mr. President, it is rather remarkable, to me, at least, that such procedure would enable the varnish to lose its tackiness. As a matter of fact the general theory, so far as I know, at least, has been that the fixing of varnish is due to oxidation. Of course it is quite possible that the filtered light that Mr. Lumbard speaks of assists in that operation, but it is also a well

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known fact that varnish may be dried off without exposure to the sun, and in practice, on automobile and carriage and furniture leather the varnish coat is not exposed to the sun at all, but is put into the ovens and heated to a temperature of approximately 180 deg., taken out of the oven, allowed to cool, and sent along. Where the under coats are properly prepared and put on oxidation simply affects the varnish coat, or the top coat. And it does not further oxidize the under coats, leaving them pliable and soft.

MR. LUMBARD: No leather manufacturer in manufacturing chrome patent has succeeded in removing tackiness by ordinary interior drying without exposing it to the sun or some light of that character. It is done, as I know, in the carriage leather industries, but in that case there is a different foundation to work on, and in manufacturing chrome patent leather for shoes, they rely entirely on a very thin film. They wish to retain as little of the japan surface directly on the grain as possible, and in that way they have had to do considerable sun drying.

THE ANALYSIS OF TANNING MATERIALS.*

By Hugh Garner Bennett, M.Sc.

PART I.—AN IMPROVED BASIC CHLORIDE SHAKE METHOD.

It is now nearly eight years since Procter and Bennett published their basic chloride shake method for the analysis of tanning materials, and that method—with trifling modifications—is still in use as the official method of the I. A. L. T. C. It is a considerable tribute to the method that during the last few years little or no alteration has been made to it, and that no marked improvement upon it has yet been suggested.

The shake method as used at present was a great step towards truth. The great number of comparative analyses now available show beyond dispute that the shake method estimates more non-tannins and less tannin, and is therefore so far nearer the actual truth.

At the same time the present official method does not yet properly distinguish between the tannin and non-tannin content of

* J. S. C. I., 33, pp. 1182-6, 1914.

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tanning materials, there being still a considerable proportion of non-tanning matters absorbed by the hide powder and reported as tannin. This has been conclusively demonstrated by the analyses of artificial mixtures, as in the experiments of Procter and Blockey (*Collegium,* 1903, 114, 124), and of Parker and Bennett (*J. S. C. I.,* 1906, 1193). In the case of some non-tannins, especially of the gallic acid and catechin type, the error even with the present method must be very considerable. Therefore, any further improvement in the method of tannin analysis should be in the direction of higher non-tannin results, and in consequence, lower results in tannin. What leather chemists must continue to search after is a method which detannizes easily and yet yields a higher percentage of non-tannins. Important financial interests are involved in this matter, but as long as leather chemists are using a method of analysis which does not yield the actual truth in its results, they must continue their endeavors to improve their method of analysis in such a way as to approach that truth. What is desired is not to estimate leather-forming value, but to determine the percentage of "tannin" in a material, whatever the nature and quality of that tannin. The tannins are a pretty definite group of compounds, and there is no doubt as to what is included in the term. Their relative leather forming value and the leather forming value of some non-tannins are certainly questions not to be forgotten, but are quite distinct from the question of the estimation of the amount of tannin.

Naturally those who sell tanning materials, especially tanning extracts, will not welcome changes which show less tannin present in those materials, but any change towards truth would apply generally; it is only those who have inferior materials to offer, who have any real need to fear an improved method of analysis. Further, it is urgently necessary from the tanners' point of view that any positive improvement and advance towards truth should be adopted as soon as possible.

The question is therefore: *what alterations in the official method will give equally good (or better) concordance, and yet estimate less tannin?* How can the absorption of non-tannins by hide powder be lessened? Some previously published experiments by the author supplied a hint towards the answer. In a

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paper on "The Standardization of Hide-Powder" (*J. S. C. I.*, 1907, 455), the influence of the texture and acidity of the powder itself was pointed out, and the importance of the acidity due to chroming was emphasized. Procter and Bennett (*J. S. C. I.*, 1906, 1203) also pointed out the influence on results of the amount of moisture added with the powder, and hence suggested a fixed amount. On similar grounds they suggested a fixed amount of hide powder. The question arises, therefore, whether the amounts fixed a few years ago were the best, and whether by a judicious alteration we might not be able to show (by substantially the same method of analysis) a distinct improvement in accuracy. The writer now suggests that the shake method would give lower tannin results, and higher non-tannins if modified in any or all of the following ways:

1. Decreased acidity in the hide powder before chroming.
2. Detannization in a more dilute infusion.
3. The use of less hide powder.
4. Decreased acidity in the hide powder due to chroming.

1. *Decreased Acidity Before Chroming.*—In a previous paper by the writer experiments were recorded with hide powders with acidities up to 12.6, as determined by the method suggested in the same paper. The great influence of this factor on the results was emphasized, and it was demonstrated that the more acid powders gave much lower non-tannin results. It was further pointed out that "if a large quantity of acid were in the powder it would be necessary to have some method of controlling it in the washing, for it would be useless to fix a definite acidity in the unchromed powder, if an indefinite proportion is to be washed out." It is nevertheless precisely this futile method that has been adopted by the I. A. L. T. C. As a first limit, the author suggested an acidity of 5.0 as a *maximum*; later A. T. Hough pointed out that hide powders with greater acidities could be brought down to 5.0 by the addition of the required amount of caustic soda solution; but more recently, on the plea of concordance, the I. A. L. T. C. have adopted the method of acidifying more neutral powders to bring their acidities up to what was previously a maximum. As pointed out above, this cannot be conducive to concordance. If a few cc. N/10 HCl are added to the powder

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before chroming—how much of this will be left in after washing?

The ordinary test for chlorides in the wash waters is no guide at all. That test was devised as an indication of the rate at which salt (NaCl) was being washed out of the powder. This was just a matter of repeated dilution until its concentration was negligible. Washing free from chlorides when the powder is acidified with hydrochloric acid is another matter altogether. That is a matter of hydrolysis, not of dilution, and in the hands of different operators is liable to be carried out to a widely different extent, with the inevitable difference in the results. The effect of acidifying the hide-powder up to 2.5 to 5.0 acidity has simply been—

1. To render the washing test of little or no value.
2. To give lower non-tans, and higher results in tannin.
3. To produce discordant results between different operators.

If the I. A. L. T. C. think the time is ripe for so standardizing the powder that its acidity should be definite and universal, it seems clear that the amount to fix on should be nil. The suggestion of Hough should be carried a stage further, and the powder made neutral by the addition of the required amount of N/10 NaOH solution. This would restore the value of the washing test for chlorides, would give far better concordance than acidified powders, and would also contribute towards the object of this investigation, *viz.*, more accurate results. The experiments recorded below confirm completely the author's statement of eight years ago that neutral powders when chromed as usual will detannize as easily and as completely as acid powders. If that be so, what need is there for any acid? It would be perfectly satisfactory to rely solely upon the acidity due to chroming for the attainment of complete detannization.

Neutralized powder is much easier to manipulate than acidified; it is easier to detach from the linen, easier to wash, and very much easier to squeeze. With acidified powder a press is practically a necessity, but with neutralized powder it is quite unnecessary.

2. *Detannization in a More Dilute Infusion.*—In the original

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paper of Procter and Bennett (*J. S. C. I.*, 1906, 1203) the amount of water to be added with the hide powder was fixed at 50 cc. to 100 cc. liquor. To avoid a factor this was later changed to 20 cc., making the total volume of liquid 120 cc., of which, half (60 cc.) were evaporated for weighing. It was observed that when the total volume was made up to 150 cc. the non-tans were slightly higher than when the total volume was 120 cc. *i. e.*, if the determination be conducted in a more dilute infusion, there is a lesser absorption of non-tanning matters. In the present work it has been sought to dilute the infusion as much as could be done conveniently, and by adding 100 cc. distilled water to 100 cc. liquor, and mixing gently before adding the hide powder for shaking. With the powder 20 cc. water are added as usual, and in this case the total volume is 220 cc., of which half, 110 cc. are evaporated by pipetting successively 60 cc. and 50 cc. of non-tan filtrate. This may be done in the usual basin, or, if desired, in special basins to contain 110 cc. The influence on the results is very marked, as will be seen from the figures below.

3. *The Use of Less Hide Powder.*—In considering the standardization of hide powder, stress was laid on the influence of the texture of the hide powder on the result, and comparative work showed that granular powders gave higher non-tannins than fibrous powders. This was doubtless to be explained by the greater surface action of the fibrous powder. Although truer results are yielded by the granular powders, they were ruled out for the sake of general concordance, and also to obtain a closer agreement with the results of the American chemists, who used fibrous powders.

In the present investigation, which seeks only to approximate to truth, another alternative presents itself. If less surface action be the cause of the difference between granular and fibrous powders, it would be an easy matter simply to reduce the amount of hide powder used, to obtain less absorption (or adsorption) of non-tanning matters. The present amount, 6.5 grams dry powder per analysis, was at the time of choice the *maximum* amount used by the American chemists, and was fixed upon by Procter and Bennett to make concordance more certain.

There seems no doubt now that this amount is quite unneces-

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sarily large, and that complete detannization can be obtained by 5 grams dry powder per analysis, and possibly even less.

A common criticism of our method of analysis has been that in analytical work the hide powder is in distinct excess over the tannin present, whereas in the tannery the tannin is in excess of the hide. Perhaps this criticism will always have some force, for analysis must do its work in a comparatively short time, yet there is every reason to make the difference as small as possible. Less hide powder would mean that the analysis was carried out nearer to tanyard conditions. On this principle, as well as to obtain higher non-tannin results, it is highly desirable that in analysis the hide powder should be in the least possible excess.

The experiments here recorded show that this factor has less influence on the results than might be expected, but it clearly has an influence, and in the required direction. In working with a decreased amount of hide powder the writer observed the convenience involved in such a change. The smaller quantity of powder was more convenient to manipulate, and much quicker to wash. The saving in cost (23 per cent.), as well as time and trouble, would be considerable in many laboratories. In short, therefore, less hide powder means truer results, in less time, with less trouble, at less cost.

4. *Decreased Acidity Due to Chroming.*—Even the basic salt $Cr_2(OH)_3Cl_3$, which is now in use for chroming, is considerably acid, and it was decided to test the effect of chroming with a more basic salt, and so reducing the acidity due to chroming. The influence of acidity before chroming is considerable, and there seemed no reason to expect the contrary in the acidity due to chroming. This indeed proved to be the case. The chromic chloride for the present experiments was made basic to correspond to the salt $Cr_2(OH)_4Cl_2$. For a few experiments only 1.89 cc. N/10 sodium carbonate may be added to each 1 cc. of the ordinary 10 per cent. stock solution of $Cr(OH)_3Cl_3$. As anticipated, the non-tannins obtained were distinctly higher when the more basic salt was used, and yet the solution was quite satisfactorily detannized. The powder was much more easily washed free from chlorides.

The following experimental results were obtained by testing

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the same sample of a good chestnut extract in various ways, and illustrate the influence of the various factors discussed above. The results are each a mean of two very closely agreeing duplicates:

Method used	Acidity before chroming	Amount of hide powder per "shake"	Total vol. of detannized solution cc.	Chroming salt	Per cent. non-tans
One factor changed	5.0	6.5	120	$Cr(OH)_3Cl_3$	11.8
	5.0	6.5	220	$Cr(OH)_3Cl_3$	12.9
	0.0	6.5	120	$Cr(OH)_3Cl_3$	12.6
	5.0	6.0	120	$Cr(OH)_3Cl_3$	11.9
Two factors changed	0.0	6.0	120	$Cr(OH)_3Cl_3$	12.6
	0.0	5.5	120	$Cr(OH)_3Cl_3$	12.6
	0.0	5.0	120	$Cr(OH)_3Cl_3$	13.0
Three factors changed	0.0	6.0	220	$Cr(OH)_3Cl_3$	13.4
	0.0	5.0	220	$Cr(OH)_3Cl_3$	13.9
Four factors changed	0.0	5.0	220	$Cr(OH)_4Cl_2$	14.9

In each of these experiments the solutions were quite completely and satisfactorily detannized, and the absorption of tan took place with the same ease as in the I. A. L. T. C. method. It will be seen that when all the factors are changed that have been discussed above, the difference from the I. A. L. T. C. method is about 3 per cent. Other extracts and other materials show other differences according to the nature of the material and the quantity of non-tanning matters associated with that particular material.

By altering the above four factors farther in the same sense, it should be possible to obtain still higher non-tannins and still more correct results. If the alterations be carried far enough, of course, the time will come when detannization will become incomplete. The most correct results will be obtained when these changes are strained almost, but not quite, to the breaking point. What exactly this point will be depends largely on which factor is pushed to the extreme limit. The author, however, regards a further reduction of hide powder to even less than 5 grams per shake as the next most desirable step. It is intended to make further experiments on these lines. It is possible that the attainment of the minimum amount of hide powder may involve some extension in the time of shaking. The author would there-

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fore suggest that the basic chloride shake method should be revised officially, and carried out with the following modifications:

1. The hide powder to be exactly neutralized before chroming.

2. Only 5 grams dry hide powder to be used instead of 6.5 grams per analysis.

3. To 100 cc. ordinary strength infusion, 100 cc. of distilled water to be added before the prepared hide powder, and the total volume made up to 220 cc., of which any convenient aliquot part may be evaporated for weighing, preferably 110 cc. as its use involves no "factor."

4. The chroming liquor to be a solution of the salt $Cr_2(OH)_4Cl_2$ instead of $Cr_2(OH)_3Cl_3$.

These alterations, though perhaps not as near the truth as it is possible to get, would at any rate be a distinct step towards that goal. Though still within the limit as to what is possible in improving the method of analysis, they might well be made part of the official method of analysis as another step towards the ideal method.

It still remains to satisfy "Concordance." The author's own experience with the revised method leads him to expect no difficulty in this direction. The same material analyzed in duplicate in successive days has given the same results. There is, however, no perfectly satisfactory way of testing the concordance of a method except by collecting the results obtained by independent observers in different laboratories, and the writer therefore cordially invites collaboration in testing this method. Although the writer considers this revised method well within the limits of complete detannization, it is just conceivable that with some particular test a trace of tan may be left unabsorbed. Any method which seeks to be nearer the truth must risk this to some extent. If incomplete detannization should be observed in any instance the defect can easily be remedied. In all the experiments hitherto the usual 15 minutes' churning has been given, but some experiments undertaken in conjunction with Mr. J. R. Blyth a few years ago indicated that the extension of the time of churning has little or no effect on the absorption of non-tannins and upon the result. By extending the time of churning 5 or 10 minutes,

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complete detannization together with all the advantages of the improved method could still be easily ensured.

If the objection be urged that the revised method needs longer time for the evaporation of 110 cc. instead of 60 cc. it may be pointed out that on the other hand time is saved in washing the powder, which needs more personal attention. Again it is questionable whether the result of the analyses would be at all retarded, for at present the "non-tannins" are quicker to finish than the "total solubles," owing chiefly to the much less time required for drying to constant weight. Further, it is possible that the time required for a whole analysis could easily be shortened by reducing the time for chroming hide powder, the one hour specified is unnecessarily long, especially with the more basic chroming liquor now suggested. In conclusion, it may be of interest to give a few comparative analyses with different tanning materials. The differences here noted vary according to the source and methods of manufacture:

Material	Tan per cent. (official method)	Tan per cent. (Bennett)	Difference per cent.
1. Sumach	24.5	23.0	1.5
2. Valonia	29.2	25.2	4.0
3. Myrabs	33.3	31.6	1.7
4. Myrabs extract	30.1	26.1	4.0
5. Chestnut	28.0	24.9	3.1
6. Oakwood	26.4	23.2	3.2
7. Quebracho (sulphited)	65.1	52.8	12.3
8. Quebracho (bleaching extract)	35.6	27.6	8.0
9. Cube gambier	46.3	36.9	9.4
10. Block gambier	31.1	23.9	7.2

PART II.—TANNERY LIQUORS.

The results of the analysis of used tan liquors, when obtained by the official method of the International Association of Leather Trades' Chemists for tanning materials, are far from trustworthy. The author has given considerable attention to this question, which has been much neglected in the past.

It has been found a great advantage to utilize the improved basic chloride method suggested in the preceding paper. The gain in accuracy is even greater with liquors than with tanning materials, on account of the relatively higher non-tannin content

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of the former. In reducing the proportion of hide powder employed and in working at a greater dilution, the improvement in accuracy is considerable. In the matter of the acidity of the hide powder, due either to its original acidity or to the chroming, the arguments have even greater force for liquors than for materials, because liquors are always so acid themselves that any acidification of hide powder is superfluous. The only point of chroming is to render the powder insoluble.

However the I. A. L. T. C. regard the improved method with respect to tanning materials, there can be no arguments of financial interest against the immediate adoption of these improvements for tannery liquors.

In the ordinary analysis of yard liquors the determination of insoluble matter is usually not required. The most convenient plan, therefore, is to filter the liquor through filter paper before dilution. If it is required to determine the insoluble matters, special care must be taken in sampling, as the distribution of the mud in a pit of liquor varies enormously. It is incorrect, moreover, to dilute the liquor and then filter it, for what is required is the amount of insoluble matter in the liquor itself, not in the liquor if it were diluted. For the "total solids," the same volume of liquor as is taken for the "solubles" and "non-tannins" should be diluted into another flask.

In the tannery, results stated in percentage by volume are of far more value than those in percentage by weight. Hence the amounts of liquor taken for dilution should be measured. The "barkometer strength" of the liquor is usually noted before analysis so that by the specific gravity it is always possible to calculate the results into percentage by weight. For the weaker liquors there is no advantage in accuracy in making one liter of diluted liquor, and there is much gain in convenience and speed by making up only half a liter, and for the weakest liquors only a quarter of a liter. Sometimes, indeed, no dilution at all is necessary. Pipettes are the best means of measuring the liquors and it is very convenient to have a set of pipettes delivering 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 75, 100, 150 and 200 cc. respectively. The liquors are delivered into the dilution flasks containing cold distilled water and made up to mark with cold

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distilled water. Hot water is unnecessary as the liquor is clear and dissolves without difficulty. In the case of strong liquors odd quantities are necessary, and a 10 cc. graduated pipette is useful in addition to those mentioned above.

As the detannization is to be carried out at a dilution of 0.2 per cent. tannin approximately it is best to dilute to this strength direct and use this solution both for the determination of the "soluble solids" and of the "non-tans."

This halving of the usual quantities involves no loss of accuracy in weighing for the residues from 50 cc. of a 0.2 per cent. tan solution of even the newest liquors of a tanyard is greater than that obtained from the "non-tannins," of some quebrachos. In the case of the older liquors this extra dilution is a great advantage as the amount of solid matter in a 0.2 per cent. tan solution increases rapidly as the liquors become older.

It is convenient also to use the same bottles, churn, and other apparatus as in the I. A. L. T. C. method, so that 100 cc. of the liquor is employed, and to detannize this only 2.5 grams dry hide powder will be required. This will weigh 7 to 9 grams when washed and pressed, so that the 100 cc. are conveniently made into 110 cc. by the addition of distilled water. To avoid a factor it is convenient to evaporate 55 cc. of the non-tan filtrate, which is equivalent to 50 cc. of the original liquor solution. Duplicate analyses, such as are usual in extract analysis, are unnecessary for liquors so that it is possible for one operator to undertake more than twice as many liquors as extracts.

Even with the improvements suggested the gravimetric method is still open to grave criticism when applied to old tan liquors which have been worked down the yard in the usual way. If solutions containing 0.2 per cent. tannin are used and 50 cc. evaporated for "soluble solids," the results are still unreliable, for it is impossible to get constant weight. Basins and residues lose from 10 to 30 mgms. at each re-weighing and the residue obviously decomposes, becoming quite black. Results in soluble solids may vary over a range of 1.5 per cent., which is absurd when one is attempting to estimate 0.5 to 1 per cent. of tan. The same inconstancy is observed in weighing the non-tannin residue, rendering the tannin result doubly uncertain. The reasons for

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this difficulty are not far to seek. There is too much residue to dry effectively in the ordinary way. Well over 1 gram of residue is sometimes obtained from 50 cc. of solution even when diluted to the extent suggested above, and it is quite impossible to dry a layer of this on the bottom of even a flat-bottomed basin. The best and simplest plan is to evaporate a smaller quantity than the usual 50 cc. For nearly spent liquors 20 cc. and 10 cc. are convenient alternatives. The gain in accuracy in this respect involves a further gain also, because the evaporation takes only a very short time comparatively and thereby eliminates the possibility of much decomposition in the heated liquor. There is also a considerable gain in speed. The author recommends as a general rule that the residues to be weighed should never exceed 0.25 gram. Whatever volume is employed for the total solids, should, for the same reasons and for convenience in calculation, be employed also for the non-tannins.

Loss of weight on drying is also connected with the chemical action of the constituents of the residue. Experiments made by the author in conjunction with Dr. J. G. Parker some years ago (*J. S. C. I.*, 1906, 1193) showed that it is impossible to evaporate mixtures of tannin and calcium acetate and obtain the theoretical results. The tannin not only expels the acetic acid, but the calcium tannate rapidly oxidizes. It may be suggested that in liquors there is excess of various acids; this is not always the case, especially in the first liquors of a yard, which often receive a great amount of lime in the course of a day's work. Furthermore, if the liquor is acid, the excess of volatile acids is driven off in evaporation, and the non-volatile acids—such as gallic acid —are just as susceptible as the tannin to similar oxidation. A simple remedy for this difficulty is to acidify the liquors (soluble solids and non-tannins) just before evaporation (not before analysis) with tartaric acid, of which 5 cc. of a 0.5 per cent. solution is employed. This acid assists materially in the complete expulsion of the volatile acids, both free and combined. It also keeps the liquor always acid and so prevents the alkaline oxidation due to lime salts with weak acids. Similarly it ensures an acid residue and so prevents the oxidation of any tannate of lime. Tartaric acid is non-volatile, and the weight used, 25 mgms., can

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be deducted from the weight of the residue. The difference in color in residues evaporated with and without the acid is very noticeable. Oxalic acid seemed at first more suitable than tartaric acid for this purpose on account of its calcium salt being insoluble even in acid solution, but with oxalic acid, however, it is impossible to obtain a residue of constant weight. Tartaric acid, on the other hand, does not decompose at 100° C., has no water of crystallization, and gives a crystalline residue of constant weight after half an hour's drying at 100° C.

Apart from the lime and other alkali salts present in tan liquors, there is probably a greater tendency to oxidation in liquor residues than in those from fresh materials, and there is therefore a strong objection to heating at 100° C. for any great length of time. The presence of tartaric acid is again of some value, for it is also a mild reducing agent and would tend to retard any such oxidation of the tannin and non-tannin residues. The author has found it a great advantage to concordance of results to limit to a definite extent the time which shall be allowed for drying residues, and has made a practice of giving one hour's drying exactly and no more. Whilst this is an advantage to concordance it is in all probability an advantage also in correctness of result, for after one hour at 100° C. the error due to water is of far less importance than the error due to decomposition and oxidation. This desirability for limited time in drying justifies also the employment of small residues.

The author therefore recommends that the analysis of tannery liquors should be carried out as follows:

The liquor is passed through filter paper until clear. A solution of the filtered liquor is made to contain between 0.17 and 0.23 per cent. tannin. The volume of clear liquor necessary for this is pipetted into a liter, half-liter, or quarter-liter graduated flask containing some distilled water. The flask is filled up to the mark with distilled water and mixed well.

To determine the *total soluble matters,* 50 cc. or less of this solution should be evaporated to dryness in flat-bottomed basins, into which 5 cc. of a 0.5 per cent. solution of tartaric acid has previously been pipetted. The weight of residue so obtained must not exceed 0.25 gram. When the solution is evaporated to

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dryness, the basin is dried in a steam oven for one hour only, and then cooled and weighed. From the weight of the residue 25 milligrams must be deducted before the percentage is calculated.

To determine the *non-tannin matters* the procedure is as follows:—The moisture of the air-dry hide powder is determined and the quantity equal to 2.5 grams actual dry hide powder is calculated. Any multiple of this quantity is taken, according to the number of analyses to be made, and wet back with 10 to 12 times it weight of distilled water. The acidity of the hide powder is determined in the usual manner, and the volume of N/10 caustic soda necessary exactly to neutralize 2.5 grams of dry hide powder is calculated. Any multiple of this quantity, according to the number of analyses being made, is added to the wet hide powder and well mixed until the mass gives no pink color when one drop of a 0.1 per cent. alcoholic solution of phenol-phthalein is added. The chroming solution is then added.

For chroming, 2 per cent. of chromic chloride ($Cr_2Cl_6 12H_2O$) on the weight of the dry hide powder is employed, its solution being made basic to correspond to the formula $Cr_2Cl_2(OH)_4$ by the addition of sodium carbonate. A 10 per cent. stock solution of this chroming liquor is very convenient and is made by dissolving 100 grams of the chromic chloride crystals in a little distilled water in a liter flask and very slowly adding a solution of 40 grams of anhydrous sodium carbonate, with constant stirring, finally making up to mark with distilled water and well mixing. Of this solution 0.5 cc. should be used for 2.5 grams dry hide powder, *i. e.*, for each analysis.

The hide powder and chrome solution are churned slowly for one hour, and the powder is then washed free from chlorides and soluble matter, as in the Procter-Bennett shake method. The silver nitrate test should be similarly employed. The hide powder is then squeezed to contain about 70 per cent. of water and the whole weighed. The amount M, containing 2.5 grams dry hide powder is thus found, weighed out, and added immediately to 100 cc. of the diluted solution of the liquor, along with (12.5—M) cc. of distilled water. The whole is corked up and agitated in a rotating churn for 15 minutes, and then squeezed immediately through linen. The liquor obtained is again filtered through

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filter paper, the filtrate is returned till clear, and 55 cc. or less (according to the amount used for the total solids) is evaporated to dryness in flat-bottomed basins into which 5 cc. of a 0.5 per cent. solution of tartaric acid has been previously pipetted. When the solution is evaporated the basin should be dried at 100° C. for one hour, cooled, and weighed. From the weight of the residue 25 milligrams must be deducted before calculation.

If the official hide powder is to be employed, the quantities to take for batch B1 are given in the following table:

No. of liquors to be analyzed	Weight of official hide powder to take (per cent.)	No. of cc. N/10 NaOH required (per cent.)	No. of cc. $Cr_2Cl_2(OH)_4$ solution required (per cent.)
1	2.85	1.4	0.5
2	5.70	2.8	1.0
3	8.55	4.2	1.5
4	11.40	5.6	2.0
5	14.25	7.0	2.5
6	17.10	8.4	3.0
7	19.95	9.8	3.5
8	22.80	11.2	4.0
9	25.65	12.6	4.5
10	28.50	14.0	5.0
11	31.35	15.4	5.5
12	34.20	16.8	6.0

The advantages claimed for this method of analysis over the I. A. L. T. C. method are:

(1) A considerable improvement both in accuracy and in concordance. This applies to the estimation of soluble solids, and of non-tannins also. The method shows distinctly less tannin than the official method.

(2) A much greater ease of execution. Both in washing the hide powder and in weighing the basins, 5 tan liquors involve less work than 1 extract done in duplicate.

(3) A considerable saving in cost. As only 2.5 grams of hide powder are used per analysis, the cost is little more than one-third that of the official method.

TANNERY PROBLEMS FOR TANNERS AND CHEMISTS.

By W. R. Cox.

Inasmuch as the first thing to be considered in the tanning process, beginning at the beam-house (and a very important one), is the water used in the soaks, we will begin here. It is generally

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conceded and has been practically proved that soft water is the best for general use in the soaking of all kinds of hides and skins. Conditions in various parts of the country are different, and some tanners do not have a large enough supply of soft water available. In consequence they have to use hard water, and are obliged to resort to various means to soften it. The chemists of the A. L. C. A. could be of material service to these tanners by going into this question and offering some easy solution, or two or three solutions, of the water softening problem, and also by showing the tanner an easy way to determine the hardness of the water he is using.

In warm weather, where soft water is used from a source whose temperature runs much above 60° F., tanners experience considerable trouble in soaking their hides long enough to get the best results in the beam-house, without some loss from putrefaction. Here is another point where the A. L. C. A. can offer suggestions to the tanner; as to the best thing to use as a preservative, which will not stop the action of the lime in plumping the hide in the beam-house. If the various tanners who have experienced the troubles mentioned above would cite some instances, so that the A. L. C. A. would have more data to work on, I think the chemists could offer advice which might do away with much of the trouble from the water question. Of course many chemists and tanners will say "Put in a water-softener." There are many plants whose capacity would hardly warrant such an expense, and the chemists should be able to make suggestions that would be of material assistance to these tanners.*

Now coming down to the beam-house proper. Tanners to-day on the whole know very little if any more than our grandfathers knew about a beam-house. Some of you may take issue with me on this statement, but when you stop to consider that tanners 30 or 40 years ago used sulphur and soda in conjunction with lime and knew what varying amounts of these different chemicals would do to produce certain results in unhairing and plumping, you will see that we are not very much further advanced when we use sulphide of sodium.

* See M. F. Corin's article in the Journal for March, 1914. Also Dr. Harrison's in the August, 1912 number Ed.

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I do not mean to imply by this that sulphide of sodium is not a good thing to use. I think it is, but I do think that where it is not used properly it is a menace both to the hide and to the resulting leather. If the chemical equation is figured out, showing the proportions of sodium sulphide, lime and calcium chloride, and these chemicals are properly mixed, it should produce calcium hydrosulphide. This is, I believe, conceded by chemists to be an ideal depilatory agent, and when made correctly it will keep without deterioration. Now we come to the point of the use of this product in the beam-house. The hides are brought into contact with this solution, and a part of the organic matter in the hide, namely, the hair, breaks down chemically, and here arises a lack of uniformity in the liming of hides and skins. For instance, the breakdown generates ammonia which has an entirely different action on the hide, dissolving the gelatin, and this action should be controlled. Now for a solution of this problem, cannot the A. L. C. A. suggest some easy, quick method which the average tanner, who possesses common sense, could use for titrating limes every morning for combined alkali, free ammonia and caustic? If this were done, and a tanner given the necessary data to work on, so that he would know whether to add more lime, sulphide or calcium chloride, so as to keep the proportions correct, better leather would be produced.

Now a word to the tanner. In the average beam-house (this is not so in all cases), there is a decided slackness. Lime is dumped into pits which are not uniform in size, and the sulphide is sometimes slaked with the lime and sometimes used by simply dissolving the sulphide and dumping it into the pits, which is wrong, as it is generally conceded that he might as well use caustic soda instead of spending the money for sulphide of sodium.

The thing that the average tanner must have brought home to him is the necessity of first doing the thing in absolutely the right way, and then to keep on doing every day in the same way, and not to have so much guess work. Some tanners prefer to use arsenic sulphide in conjunction with lime, and some use arsenic, sodium sulphide and lime. The chemist here could do a good turn to the tanner by explaining to him in exact terms

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just what he produces when he makes these different mixtures, and why; why some of them are wrong from a chemical standpoint, and why some of them are right.

The length of time used in liming varies, and I think I may say without danger of correction that this difference is due more to the whims of the tanner than to any reason he can give as to why he limes three days, or in some cases, ten. In making some kinds of chrome leather it is necessary to preserve as much of the hide-substance as possible. The question of chrome tanning is merely a question of fixing or precipitating chrome on the fibers of the hide in varying percentages, from 2.5 per cent. in the case of calf-skins up to 6 per cent. or even 8 per cent. in the case of chrome sole leather. For glove leather, where softness and stretch are absolutely necessary to make a marketable piece of leather, high liming and low bating are perhaps necessary, but in other leathers these three factors, namely, soaking, liming and bating, play the biggest part in the character of the finished leather. The importance of these three things is, however, often overlooked by the tanner, and mistakes in them he endeavors to cover up in the tanning, fat-liquoring and finishing, and then he is dissatisfied with the yield, the plumpness or the general characteristics.

I think this will be sufficient for this number, but now I should like to see the chemists enter into a general discussion with the tanners on some of the points which have been brought out here. By no means all the problems are here; just a few of them; but with open and frank discussion you will be able to arrive at some very good remedies.

I should like to see some of the chemists present through the columns of the JOURNAL some suggestions for the questions stated above, namely, on the softening of water, preservative in warm weather, method of titrating limes when they contain sodium sulphide, lime and calcium chloride; also a method of titration where arsenic sulphide and lime are used. I wish too that the chemists would give the tanners an explanation as to what chemical substances are formed when they mix these different articles in varying proportions, and explain to them in fairly simple language why such chemical changes take place.

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ABSTRACTS.

Experiments with Neradol D. ALLEN ROGERS, *Reports of Third Year, Tanners' Institute,* pp. 25-30. Hides unhaired with lime were split into sides, one side of each being thrown into water over night and the other into a neradol solution of 6° bk. for the same length of time. The packs were then started together into the yard. Samples were cut from each lot at intervals and analyzed for hide-substance. These samples were air dried and then heated 3 hours at 105° C. Results from two series are shown in the table.

Date	Hide-substance, per cent. With neradol D	Straight
SERIES 1.		
Feb. 11	67.47	71.68
Feb. 18	64.99	69.24
Feb. 24	58.61	62.95
Mar. 4	53.00	56.78
Mar. 11	44.21	52.02
SERIES 2.		
Feb. 21	81.31	83.49
Feb. 24	73.80	74.71
Feb. 27	69.72	68.39
Mar. 9	65.71	59.44
Mar. 16	54.71	53.24
Mar. 23	52.14	51.67
Mar. 31	51.15	51.46
Apr. 6	51.05	50.07

The color of the sides treated with neradol D was lighter than the others. While the absorption of tanning material in the case of the sides treated with neradol is more rapid at first, the total amount of leather produced at the end of tannage is the same in the two cases. The leather made with preliminary treatment with neradol was tough, with a good, firm grain.

Tests on Neradol D. G. J. LAEMMLE, H. J. NEWMAN AND M. W. SHEPARD. *Reports of Third Year, Tanners' Institute,* pp. 38-42. Four pieces of calf-skin, pickled as for chrome tannage, each weighing about 70 grams, were used. One piece was drummed on the shaker for 1 hour each in a series of liquors made from straight quebracho extract, of 6°, 8°, 12°, 15°, and 20° bk., respectively. A second piece was similarly treated with a series of straight neradol liquors of the same barkometer strengths as the quebracho. A third piece was treated with a series of quebracho liquors like the first series, but with an amount of neradol added to each equal to 5 per cent. of the weight of the piece of skin. Analyses of the four pieces of partly tanned skin and of the untanned piece are given in the table.

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	Original pelt	Quebracho tannage	Neradol D tannage	Combination tannage
Fat, per cent.....	0.464	0.377	0.8283	0.6
Hide substance, per cent.....	89.0	71.25	77.28	58.91
Ash, per cent.....	1.548	0.1233	1.785	0.441
Dry weight of original sample, grs..		23.15	14.2	16.47
Dry finished weight, grams.....		30.34	16.25	22.47
Per cent. gain		131.0	116.4	136.5
Pelt hide substance in grams		20.6	12.62	14.65
Hide substance in grs. in tanned leather		21.6	12.78	13.25

Efforts to analyze the liquors gave results so unsatisfactory that they are not published. A second experiment was made, using two lots, six each, of pickled sheep-skins. One lot was drummed in a neradol solution of 6° bk. for 1 hour and allowed to lie in it over night. The skins were then drummed for 1½ hours in a liquor of 30° bk. made up of hemlock and chestnut in equal parts. Samples were then taken and the drum run for 1½ hours; other samples taken, and the drum again run for 1 hour, when tannage was found to be complete. The six skins which had not been treated with neradol were tanned in precisely the same manner, but at the end of 4 hours they were found to be under-tanned. A fresh liquor was then made up like the first, and they were run 1½ hours in that, when tannage was found to be complete. Both lots were washed, fat-liquored with sulphonated castor oil, pressed, shaved and dried. The skins treated with neradol gave a softer, plumper and fuller leather than the others. The table shows percentage of hide-substance in the two lots at various stages.

Stage of tannage	Neradol D per cent.	Straight per cent.
Original pelt	72.4	72.75
Out of Neradol D.....	71.8	—
After 1½ hours....	50.83	49.5
After 3 hours.....	48.2	48.2
After 4 hours.....	48.2	46.25
After 5½ hours.....		38.2
After shaving	51.7	56.4

Fat Content of Skins at Different Stages of the Tanning Operation. F. V. TEMPLE. *Third Year Reports, Tanners' Institute,* pp. 42-45. Fat was determined at various stages by extraction with sulphuric ether in the case of each of several kinds of hides and skins, unhaired by various methods.

Chrome Liquors. T. L. ROVELSTAD AND F. W. FEAR, *Third Year Reports, Tanners' Institute,* pp. 45-50. Three liquors were made up, in which the chrome compounds present were assumed to be $Cr_2(OH)_2(SO_4)_2$, $Cr_2(OH)_4SO_4$ and a compound halfway between these. The proportions of Cr and SO_4 for these are stated as 52 to 96, 52 to 48 and 50 to 72 respectively. Sides were treated in the drum with these liquors. The

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liquors as used contained about 2.5 per cent. Cr_2O_3. After drumming for 2 hours, the stock was neutralized and allowed to lie in the liquor over night. It is not stated what kind of skins were used. The most basic of the liquors mentioned would not tan, as the chrome precipitated out. Results with the other two liquors seem to have been nearly alike, except that absorption of chrome was more rapid in the earlier stages with the less basic liquor. The results of the leather analysis are stated in terms of $K_2Cr_2O_7$ instead of Cr_2O_3. Several methods were used. The sodium peroxide fusion method, essentially as described in the January JOURNAL, top of p. 51, was found satisfactory.

Philippine Hand-Made Shoe Industry. J. F. BOOMER, Correspondent, Manila, in *Daily Consular and Trade Reports.* It is estimated that the town of Mariquina, in the Province of Rizal, is losing over $35,000 a month through the decrease in and demoralization of its shoe industry as a result of the depression caused by the European war. Since the first of August nearly 1,000 hands have been out of work. Before the depression made itself felt there were in the village 120 small shoemaking establishments, employing 7 to 30 hands each. The gross monthly sales of the manufactured product amounted, as stated, to more than $35,000, and the shops gave employment to over 900 persons earning $0.50 to $1.25 per day. The product of these shops was marketed in Manila and the nearby Provinces. Statistics show the following distribution: To Batangas, $2,000; to the Camarines, $5,000; to Cebu, $5,000; to Iloilo, $6,000; to Pangasinan, $2,500; to Manila and elsewhere, $1,700. For the past year there has been a gradual falling off of the trade of these shops, until now practically all are closed. About the only ones that remain in operation are those having contracts for supplying the constabulary of the Province of Rizal with shoes. In Mariquina, shoemaking is practically a household industry. Little machinery is employed, except in a few instances where sewing machines are used for putting together the uppers, but even this work is done for the most part by hand. The carabao sole leather used is obtained mainly from Mecauayan, Bulacan Province. Camachile bark is used in the tanning process, giving to the leather the peculiar and, to many foreigners, offensive odor that characterizes the Mariquina shoes. Nearly all of the leather for the uppers comes from the United States, being a good willow calf obtained from a Boston firm. The prices of Mariquina shoes range from $2 to $6. The $2 shoes are sold chiefly through Chinese stores in Manila. The Mariquina shops have been supplying what is regarded as a very durable shoe to the constabulary for $3.23, the manufacturers agreeing to make all repairs free of charge where the cause is any defect in the quality of the goods.

Pine-twig Extract. RICHARD RIEDER. *Ledertechnische Rundschau* Dec. 3, 1914, pp. 345-50. The writer is a member of the firm of R. Rieder & Peratoner, Frankfurt a. M., makers of machinery and apparatus. He gives somewhat detailed plans for an installation to utilize the refuse of pine trees ("Fichtenreisig") in the manufacture of tanning extract. After

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stating that the scarcity of imported tanning materials due to the war makes it very important to utilize all possible sources of tannin native to Germany and Austria-Hungary, the author gives analyses by vonSchroeder of the twigs of the pine, as follows:

	Tannin per cent.	Sugar per cent.
Twigs with needles, up to ½ cm. size, from a tree about 30 years old.....	7.03	4.53
The same from a stunted 80-year tree	6.10	4.11
The same from a straight, well-grown 80-year tree	5.22	4.08
Top twigs of the last up to 1 cm. in size	4.37	4.59

The proportion of sugar to tannin is more than twice as great as in pine-bark extract, a fact which would make an extract of twigs alone unsuitable for ordinary tannage. By combining this with an extract low in non-tannins, such as quebracho, a very serviceable tanning material would be produced. It is possible, also, by using suitable precautions, to make good leather with the pine-twig extract alone. The extract of pine bark has been used of recent time unmixed with other material, as oak has been used since ancient times, in the making of excellent sole leather. Both of these are high in non-tannins. Liquors made from the twig extract alone would quickly become sour, and if they were to be used for the manufacture of upper leather some means of checking the acid fermentation must be used. The author suggests that they should be used first in the layers, since by the time the leather has reached this stage it is sufficiently tanned not to swell further by the high acidity of the liquors. The used liquors could then be boiled to expel the acetic acid before using them in the handlers. Here they could be mixed with a larger or smaller proportion of fresh liquor in order to produce a greater or less degree of swelling, as desired. The author estimates that an extract of 22 to 24 per cent. tannin can be made for 10 marks per 100 kilograms (about $1.10 per 100 pounds). He estimates that the waste from the yearly harvest of pine timber in Germany would yield some 4,000,000 tons of liquid extract of the strength mentioned, which is more than the present entire consumption of tanning material in the empire. (These figures for possible production appear to the translator incredibly large.) As a by-product the oil of pine needles would appear, and as it has a considerable value, the cost of the extract would be thereby somewhat reduced. L. B.

Research Laboratory Needed for American Leather Industries. EDITORIAL, *Hide and Leather,* Jan. 9, 1915. After commenting on the establishment of the Procter International Research Laboratory, the writer expresses the opinion that such a laboratory is needed in this country. The burden of financing such an enterprise should be borne not alone by the tanners, but should be shared by those who manufacture leather into shoes and other articles, since any improvements in the making and finishing of leather must benefit all who are in any way concerned with it.

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DIED.

Charles S. Forsyth, President of the Forsyth Leather Co., and an associate member of the A. L. C. A., died November 7, 1914.

CHANGE OF CHAIRMANSHIP.

Mr. J. S. Rogers having resigned as chairman of the Committee on the Determination and Estimation of Tanning Materials in Admixture, Mr. A. C. Orthmann has been appointed in his stead.

A. L. C. A. METHODS, 1915.

OFFICIAL METHOD OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION FOR THE ANALYSIS OF VEGETABLE MATERIALS CONTAINING TANNIN.

I. Raw and Spent Materials.

(1) CAUTION:

Proper care must be taken to prevent any change in the water content of raw materials during the sampling and preliminary operations. (See "general" under Sampling.)

(2) PREPARATION OF SAMPLE:

The sample must be ground to such a degree of fineness that the entire sample will pass through a sieve of 20 meshes to the inch (linear).

(a) The temperature used for drying samples of spent material for grinding must not exceed 60° C.

(b) Samples of raw material too wet to be ground may be dried before grinding as in (a). In this case a preliminary

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water determination must be made according to (IV) on the sample as received. If the portion of the sample taken for the water determination is in pieces too large to dry properly, it is permissible to reduce these to smaller size as rapidly and with as little loss of water as possible.

(3) WATER DETERMINATION:

Ten grams of the ground material shall be dried in the manner and for the period specified for evaporation and drying in extract analysis (see IV).

(4) AMOUNT OF SAMPLE TO BE EXTRACTED:

Such an amount of raw material shall be extracted as will give a solution containing as nearly as practicable 0.4 gram tannin to 100 cc. (not less than 0.375 or more than 0.425). Of spent materials such an amount shall be taken as will give a solution of as nearly as practicable the above concentration.

(5) EXTRACTION:

Extraction shall be conducted in an apparatus consisting of a vessel in which water may be boiled and a container for the material to be extracted. This container shall be provided above with a condensation chamber so arranged that the water formed from the condensed steam will drip on the material to be extracted, and provided below with an arrangement of outlets such that the percolate may either be removed from the apparatus or be delivered to the boiling vessel. The boiling vessel must be so connected that it will deliver steam to the condensation chamber and that it may receive the percolate from the container. The condensation water from the condenser must be at approximately the boiling temperature when it comes in contact with the material to be extracted.

The material of which the boiling flask is composed must be inert to the extractive solution. Suitable provision must be made for preventing any of the solid particles of the material from passing into the percolate.

(A) Woods, Barks and Spent Materials:

Five hundred cc. of the percolate shall be collected outside in approximately 2 hours and the extraction continued with 500 cc. for 14 hours longer by the process of continuous extraction

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with reflux condenser. The applied heat shall be such as to give by condensation approximately 500 cc. in 1½ hours.

(B) Materials Other than Woods, Bark and Spent:

Digest the material in the extractor for 1 hour with water at room temperature and then extract by collecting two liters of percolate outside in approximately 7 hours.

(6) ANALYSIS:

The percolate shall be heated at 80° C., be cooled, made to the mark and analyzed according to the official method of extracts.

II. Analysis of Extracts.

(7) AMOUNT AND DILUTION FOR ANALYSIS:

(A) Fluid Extracts:

Fluid extracts shall be allowed to come to room temperature, be thoroughly mixed, and such quantity weighed for analysis as will give a solution containing as nearly as possible 0.4 gram tannin to 100 cc. (not less than 0.375 nor more than 0.425). Precautions must be taken to prevent loss of moisture during weighing. Dissolve the extract by washing it into a liter flask with 900 cc. of distilled water at 85° C.

Cooling:

(a) The solutions prepared as above shall be cooled rapidly to 20° C. with water at a temperature of not less than 19° C., be made to the mark with water at 20° C. and the analysis proceeded with at once, or

(b) The solution shall be allowed to stand over night, the temperature of the solution not being permitted to go below 20° C., be brought to 20° C. with water at not less than 19° C., be made to the mark with water at 20° C. and the analysis proceeded with.

(B) Solid and Powdered Extracts:

Such an amount of solid or powdered extract as will give a solution of the strength called for under liquid extracts shall be weighed in a beaker with proper precautions to prevent change of moisture. One hundred cc. of distilled water at 85° C. shall be added to the extract and the mixture placed on the water-bath, heated and stirred until a homogeneous solution is obtained. When dissolved, the solution shall immediately be washed into a

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liter flask with 800 cc. of distilled water at 85° C., be cooled, etc., as under (A) above.

NOTE: It is permissible to make up 2 liter instead of 1 liter solutions, dissolving by washing into flask with 1,800 cc. water at 85° C. in case of fluid extracts and 1,700 cc. water at 85° C. in case of solid or powdered extracts.

(8) TOTAL SOLIDS:

Thoroughly mix the solutions; pipette 100 cc. into tared dish, evaporate and dry as directed under "Evaporation and Drying." (See IV.)

(9) WATER:

The water content is shown by the difference between 100 per cent. and the total solids.

(10) SOLUBLE SOLIDS:

S. & S. No. 590, 15 cm. single, pleated, filter paper shall be used for the filtration.

The kaolin used shall answer the following test: 2 grams kaolin digested with 200 cc. of distilled water at 20° C. for 1 hour shall not give more than 1 mg. of soluble solids per 100 cc., and shall be neutral to phenolphthalein. To 1 gram kaolin in a beaker add sufficient solution to fill the paper, stir and pour on paper. Return filtrate to paper when approximately 25 cc. has collected, repeating operation for 1 hour, being careful to transfer all kaolin to the paper. At the end of the hour remove solution from filter paper, disturbing the kaolin as little as possible. Bring so much as needed of the original solution to exactly 20° C. as described under (7), refill the paper with this solution and begin to collect the filtrate for evaporating and drying so soon as it comes CLEAR. The paper must be kept full and the temperature of the solution on the filter must not fall below 20° C. nor rise above 25° C. during this part of the filtration. The temperature of the solution used for refilling the paper must be kept uniformly at 20° C. and the funnels and receiving vessels must be kept covered.

Pipette 100 cc. of clear filtrate into tared dish; evaporate and dry as under (8).

(11) INSOLUBLES:

The insoluble content is shown by the difference between the

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total solids and the soluble solids, and represents the matters insoluble in a solution of the concentration used under the temperature conditions prescribed.

(12) NON-TANNINS:

The hide powder used for the non-tannin determination shall be of wooly texture well delimed and shall require between 12 and 13 cc. of N/10 NaOH to neutralize 10 grams of the absolutely dry powder.

(a) Digest the hide powder with 10 times its weight of distilled water till thoroughly soaked. Add 3 per cent. of chrome alum $(Cr_2SO_4)_3K_2SO_424H_2O$, in 3 per cent. solution calculated on the weight of the air-dry powder. Agitate frequently for several hours and let stand over night. Squeeze and wash by digesting with 4 successive portions of distilled water, each portion equal in amount to 15 times the weight of the air-dry powder taken. Each digestion shall last for 15 minutes, and the hide powder shall be squeezed to approximately 75 per cent. water after each digestion except the last, a press being used if necessary. The wet hide powder used for the analysis shall contain as nearly as possible 73 per cent. of water, not less than 71 per cent. nor more than 74 per cent. Determine the moisture in the wet hide powder by drying approximately 20 grams. (See IV.) To such quantity of the wet hide as represents as closely as practicable 12½ grams (not less than 12.2 nor more than 12.8) of absolutely dry hide add 200 cc. of the original analysis solution and shake immediately for 10 minutes in some form of mechanical shaker. Squeeze immediately through linen, add 2 grams of kaolin (answering test described under (9)) to the detannized solution and filter through single folded filter (No. 1F Swedish recommended) of size sufficient to hold the entire filtrate, returning until clear. Pipette 100 cc. of filtrate into tared dish, evaporate and dry as in (8).

The weight of the non-tannin residue must be corrected for the dilution caused by the water contained in the wet hide powder.

Funnels and receiving vessels must be kept covered during filtration. Flasks graduated to deliver 200 cc. are recommended for measuring the analysis solution to be detannized.

(b) Digest the hide powder with the amount of water and

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add the amount of chrome alum in solution directed under (a).

Agitate in some form of mechanical shaker for 1 hour and proceed immediately with washing and subsequent operations as directed under (a).

NOTE: In order to limit the amount of dried hide powder used, determine the moisture in the air-dry powder and calculate the quantity equal to 12½ grams of actual dry hide powder. Take any multiple of this quantity according to the number of analyses to be made, and after chroming and washing as directed, squeeze to a weight representing as nearly as possible 73 per cent. of water. Weigh the whole amount and divide by the multiple of the 12½ grams of actual dry hide powder taken to obtain the weight of wet hide powder for 200 cc. of solution.

(13) TANNIN:

The tannin content is shown by the difference between the soluble solids and the corrected non-tannins, and represents the matters absorbable by hide under the conditions of the prescribed methods.

III. Analysis of Liquors.

(14) DILUTION:

Liquors shall be diluted for analysis with water at room temperature so as to give as nearly as possible 0.7 gram solids per 100 cc. of solution. Should a liquor be of such character as not to give a proper solution with water of room temperature it is permissible to dilute with water at 80° C. and cool rapidly as described under (7, A, a).

(15) TOTAL SOLIDS:

To be determined as in Extract Analysis.

(16) SOLUBLE SOLIDS:

To be determined as in Extract Analysis.

(17) INSOLUBLES:

Determined as in Extract Analysis.

(18) NON-TANNINS:

To be determined by shaking 200 cc. of solution with an amount of wet chromed hide powder, containing as nearly as possible 73

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per cent. water, corresponding to an amount of dry hide powder shown in the following table:

Tannin range per 100 cc.	Dry powder per 200 cc.
0.35——0.45 gram	9.0——11.0 grams
0.25——0.35 gram	6.5—— 9.0 grams
0.15——0.25 gram	4 0—— 6.5 grams
0.00——0.15 gram	0.0—— 4.0 grams

Solutions to be shaken for non-tannins as in Extract Analysis and 100 cc. evaporated as in Extract Analysis.

IV. Temperature, Evaporation and Drying, Dishes.

(19) TEMPERATURE:

The temperature of the several portions of each solution pipetted for evaporating and drying, that is, the total solids, soluble solids and non-tannins must be identical at the time of pipetting.

(20) EVAPORATION:

All evaporations and drying shall be conducted in the form of apparatus known as the "Combined Evaporator and Dryer" at a temperature not less than 98° C. The time for evaporation and drying shall be 16 hours.

(21) DISHES:

The dishes used for evaporation and drying of all residues shall be flat-bottomed glass dishes of not less than 2¾ inches diameter nor more than 3 inches in diameter.

V. Determination of Total Acidity of Liquors.

(22) REAGENTS:

(a) One per cent. solution of gelatine neutral to hematine. The addition of 25 cc. of 95 per cent. alcohol per liter is recommended to prevent frothing. If the gelatine solution is alkaline, neutralize with tenth normal acetic acid and if acid neutralize with tenth normal sodium hydroxide.

(b) Hematine. A solution made by digesting hematine in cold neutral 95 per cent. alcohol in the proportion of ½ gram of the former to 100 cc. of the latter.

(c) Acid washed kaolin free from soluble matters.

(d) Tenth normal sodium hydroxide.

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DIRECTIONS:

To 25 cc. of liquor in a cylinder that can be stoppered, add 50 cc. of gelatine solution, dilute with water to 250 cc., add 15 grams of kaolin and shake vigorously. Allow to settle for at least 15 minutes, remove 30 cc. of the supernatant solution dilute with 50 cc. of water and titrate with tenth normal soda using hematine solution as the indicator. Each cc. tenth normal soda is equivalent to 0.2 per cent. acid as acetic.

VI. General.

(23) When materials containing sulphite-cellulose extract are analyzed, the fact that the material contains sulphite-cellulose extract shall be noted on the report.

(24) The test for the presence of sulphite-cellulose in a liquor or extract shall be as follows: Five cc. of a solution of analytical strength shall be placed in a test-tube, 0.5 cc. aniline added and the whole well shaken; then 2 cc. of strong hydrochloric acid added and the mixture again shaken. If at least as much precipitate remains[1] as is obtained when a comparison solution prepared as below is similarly treated, the material shall be held to contain sulphite-cellulose.

The comparison solution shall consist of sulphite-cellulose in the proportion of one part total solids to 2,000 cc. of solution, and as much tanning material, similar to that being tested, but known to be free from sulphite-cellulose, as will make up the solution to analytical strength.

(25) On public analytical work by members of this Association, the fact that the Official Method has been used, shall be so stated.

OFFICIAL METHODS FOR SAMPLING TANNING MATERIALS.

GENERAL:—

Extract whether liquid or solid, and tanning materials in general all contain moisture. The amount of moisture varies with climatic conditions, but especially in liquid, and in most solid extracts becomes less as the extract is exposed to the air. As the value of any material shown by analysis is directly dependent upon the amount of moisture contained, and as an ex-

[1] Neradol D gives the same reaction.

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posure of a comparatively few moments may alter appreciably the amount of moisture it is apparent that the sampling in all its details should be done as quickly as consistent with thoroughness and with great care to expose the material as little as possible to the air. The portions taken as samples should be placed at once in containers as nearly air tight as possible, and preferably of glass. Wood, cardboard, poorly glazed crockery, etc., are all porous and more or less absorbent and not suitable for retaining samples.

Liquid extract cannot be accurately sampled when it contains any frozen material. A sample of extract taken after live steam has been run into the extract has not the same concentration as the original extract. A sample of spent bark which has been standing where dust from fresh ground bark has sifted into it does not represent the degree of extraction of the spent bark. Samples of liquor which have been kept with no preservative in them for some time do not represent the condition of the liquor when sampled.

All extracts and crude tanning materials shall be sampled as nearly as possible at time of weighing, and for every 50,000 pounds, or less, sampled a sample shall be drawn.

(1) SOLID, POWDERED AND PASTY EXTRACTS:

The number of packages to be sampled out of a given lot shall be ascertained by taking a percentage of the total number of packages in the lot obtained in the following manner:—Divide the total number of packages by 100, multiply by 0.02 and subtract from 4.

Thus
$$4{,}700 \div 100 = 47$$
$$47 \times 0.02 = 0.94$$
$$4 - 0.94 = 3.06 \text{ per cent.}$$
$$4{,}700 \times 0.0306 = 144 \text{ Packages.}$$

Provided that for lots of 200 packages and under 5 per cent. of the number of packages shall be sampled, and for lots of 10,000 packages and over 2 per cent. of the number of packages shall be sampled.

Whenever possible every Nth package shall be set aside for sampling while the extract is being moved. When this is not

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possible, the packages shall be selected from as uniformly distributed parts of the bulk as possible.

Sample of as nearly equal size as practicable shall be taken from each package and these samples shall represent as nearly as may be, proportionally the outer and inner portions of the extract. These sub-samples shall be placed in a clean, dry closed container. When sampling is completed, the whole composite sample shall be broken up until it will pass through a sieve of 1-inch mesh; it shall be reduced to the required bulk by successive mixings and quarterings. From this bulk duplicate samples of at least 6 ounces shall be drawn from opposite quarters by means of a small flat scoop (and not by selecting a handful here and there). The sample shall be enclosed in the smallest clean, dry, glass receptacle, sealed and properly labeled.

NOTE:—Whenever possible the sample should be wrapped in paraffine paper and placed in the smallest straight-side glass receptacle, especially is this desirable during the warmer months of the year.

Sampling at place of manufacture shall be conducted by running a portion from the middle of each strike into a mold holding at least 2 pounds. These sub-samples shall be preserved with proper precautions against evaporation, and be sampled for analysis as above.

(2) LIQUID EXTRACTS IN BARRELS:

The number of barrels of extract to be sampled out of any given lot shall be not less than 10 per cent. of the whole number of barrels for every 50,000 pounds or fraction thereof. The barrels to be sampled shall be rolled and shaken from end to end until the contents are homogeneous. Whenever this is not possible the heads of the barrels shall be removed and the contents stirred until homogeneous, a sample of equal size to be taken from each barrel. These sub-samples shall be put together in a suitable closed container and be thoroughly mixed. From this bulk duplicate samples of at least 4 ounces shall be drawn and preserved in clean, dry, glass containers; sealed and labeled with such distinguishing marks as may be necessary.

(3) LIQUID EXTRACT IN BULK:

The extract shall be agitated with air, be plunged or be mixed

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by some other efficient means until homogeneous. Equal samples shall then be taken from different parts of the bulk, be placed in a proper container, be thoroughly mixed and sampled as described in (2).

(4) LIQUID EXTRACT IN TANK CARS:

The following methods are permissible:

(a) The extract shall be unloaded into clean, dry containers and sampled according to (3); or,

(b) The extract shall be mixed until homogeneous, by plunging through the dome or other effective means, then numerous equal samples shall be taken from as widely scattered parts of the bulk as possible. These samples shall then be placed in a suitable container, be mixed and sampled as in (2).

NOTE:—As it is almost impossible to secure a homogeneous mixture of the extract in a tank car, this method should be used only when no other is possible. Or,

(c) The extract shall be sampled as follows while the car is being unloaded:—A quart sample shall be taken from the discharge three minutes after the extract has begun to run; another quart sample shall be taken 3 minutes before the extract has all run out, and 3 other quart samples shall be taken at equal intervals between these two. These 5 samples shall be transferred to a suitable container as soon as taken, be thoroughly mixed and sampled as in (2).

(5) CRUDE TANNING MATERIALS:

(A) Shipments in bags, mats or other similar packages.

A number of packages shall be sampled representing 2 per cent. of the weight for every shipment of 50,000 pounds or fraction thereof, by taking representative portions from each package. These sub-samples shall be mixed together and the bulk be reduced by mixing and quartering to the desired size. Duplicate samples of not less than 5 pounds each shall be preserved in air-tight containers properly labeled.

(B) Shipments in bulk, bark, wood, etc., in sticks.

Sticks shall be taken from at least ten uniformly distributed parts of the bulk, be sawed completely through and the sawdust thoroughly mixed and sampled as in "A."

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(C) Materials prepared for leaching.

Samples of equal size shall be taken at uniform intervals as the material enters the leach and be kept in a suitable container till sampling is completed. This bulk shall then be thoroughly mixed, be reduced by mixing and quartering, and duplicate samples for analysis of at least 2 pounds in size be preserved in air-tight containers, as in "A."

(6) SPENT MATERIAL FROM LEACHES:

Samples of spent material shall be taken from the top, middle and bottom, and in each case from the center and outer portions of the leach. These sub-samples shall be thoroughly mixed, be reduced in bulk by mixing and quartering, and duplicate samples of at least 1 quart in size be preserved for analysis.

(7) TANNING LIQUORS:

The liquor shall be mixed by plunging or other effective means till homogeneous and then samples of at least 1 pint be taken for analysis. The addition of 0.03 per cent. of thymol or other suitable anti-ferment to the sample is essential to keep the liquor from altering its original condition.

When routine samples are taken from day to day and a composite sample analyzed, samples of equal size shall be taken from each vat after thorough mixing, be preserved in covered containers in as cool a place as possible, and be kept from fermentation by the addition of suitable anti-ferment, as above. This bulk shall be mixed till homogeneous and samples of not less than 1 pint each be preserved for analysis.

When a sample is taken by a member of this Association in accordance with the above method, it is requested that he state upon the label of the sample submitted and upon the analysis blank that "this sample has been taken in accordance with the official method of sampling of The American Leather Chemists Association."

OFFICIAL METHOD FOR LEATHER ANALYSIS.

(1) PREPARATION OF SAMPLE:

The sample of leather for analysis shall be reduced to as fine a state of division as practicable, either by cutting or grinding.

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(2) MOISTURE:

Dry 10 grams of leather for 16 hours at a temperature between 95°-100° C.

(3) FATS:

Extract 5 to 10 grams of air-dry leather in a Soxhlet apparatus until free from grease, using petroleum ether boiling below 80° C. Evaporate off the ether and dry to approximately constant weight.

Or, if preferred, extract 30 grams of leather as described above. In the latter case, the extracted leather, when freed of solvent, may be used for the determination of water-soluble material.

(4) ASH:

Incinerate 10 to 15 grams of leather in a tared dish at a dull red heat until carbon is consumed. If it is difficult to burn off all the carbon treat the ash with hot water, filter through an ashless filter, ignite filter and residue. Add the filtrate, evaporate to dryness and ignite.

(5) WATER-SOLUBLE MATERIAL:

Digest 30 grams of leather in a percolator over night, then extract with water at 50° C. for 3 hours. The total volume of solution to be 2 liters. Determine total solids and non-tannins according to the Official Method for extract analysis.

(6) GLUCOSE:

SOLUTIONS.

Copper Sulphate.—Dissolve 34.639 g. of $CuSO_4.5H_2O$ in distilled water and dilute to 500 cc. Filter through asbestos.

Alkaline Tartrate Solution.—Dissolve 173 g. of Rochelle salt and 50 g. NaOH in water and dilute to 500 cc. Allow to stand 2 days and filter through asbestos.

Normal Lead Acetate Solution.—Prepare a saturated solution of normal lead acetate.

DETERMINATION.[1]

Place 200 cc. of leather extract of analytical strength in a

[1] The rate of heating of the Bunsen burner used should be regulated before sugar determinations are started. This is best done by adjusting the burner so as to bring 25 cc. copper soln. + 25 cc. alk. tartrate soln. + 50 cc. H_2O in a 400 cc. beaker to 100° C. in exactly four minutes.

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½-liter flask add 25 cc. of a saturated solution of normal lead acetate, shake frequently (5-10 min.), and filter. (The funnels and beakers must be kept covered to prevent evaporation.) Add to the filtrate an excess of solid potassium oxalate. Mix frequently for 15 minutes and filter, returning the filtrate until clear. Pipette 150 cc. of this filtrate into a 600 cc. Erlenmeyer flask, add 5 cc. of concentrated HCl and boil under a reflux condenser for 2 hours. Cool, neutralize (place a small piece of litmus paper in the flask) with anhydrous sodium carbonate, transfer to a 200 cc. graduated flask and make to volume. Filter through a double filter. (The filtrate must be clear.) Determine the dextrose in the solution immediately.

Place 25 cc. of the copper solution and 25 cc. of the alkaline tartrate solution in a 400 cc. beaker. Add 50 cc. of the clarified and neutralized solution above mentioned and heat to boiling in *exactly 4 minutes* and boil for 2 minutes. Filter immediately without diluting, *through asbestos,*[2] wash thoroughly with hot[2] water, then with alcohol, and finally with ether; dry ½ an hour in water oven and weigh as cuprous oxide, determine the amount of dextrose by the use of Munson and Walker's table (Bull. 107 Rev. Bu. of Chem., p. 243) and report in percentage on leather.

(7) NITROGEN:

Gunning modification of the Kjeldahl Method, A. O. A. C. Bulletin, No. 107 (1907).

REAGENTS.

Standard Acid Solutions.—Hydrochloric or sulphuric acid the absolute strength of which has been accurately determined. For ordinary work half normal acid is recommended. For work in determining very small amounts of nitrogen, tenth normal is recommended. In titrating mineral acid against hydroxide solution use cochineal as indicator.

Standard Alkali Solution.—The strength of this solution relative to the acid must be accurately determined; tenth normal solution is recommended.

[2] The finely divided, long-fibered asbestos to be used in the glucose determination should be digested with HNO_3, washed, then digested with NaOH and washed. When gooch filters are prepared, they should be washed with boiling Fehling's solution then with HNO_3. The mats thus prepared can be used for a long time.

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Sulphuric Acid.—The sulphuric acid used should have a specific gravity of 1.84 and be free from nitrates and also from ammonium sulphate.

Sodium Hydroxide Solution.—A saturated solution of sodium hydroxide free from nitrates.

Potassium Sulphate.—This reagent should be pulverized before using.

Indicator.—A solution of cochineal is prepared by digesting and frequently agitating 3 grams of pulverized cochineal in a mixture of 50 cc. of strong alcohol and 200 cc. of distilled water for a day or two at ordinary temperature; the filtered solution is employed as indicator.

DETERMINATION.

Place 0.7 gram leather in a digestion flask. Add 10 grams powdered potassium sulphate and from 15 to 25 cc. (ordinarily about 20 cc.) of concentrated sulphuric acid. Place the flask in an inclined position and heat below the boiling point of the acid from 5 to 15 minutes or until frothing has ceased (a small piece of paraffine may be added to prevent extreme foaming).

Then raise the heat and boil briskly until the liquid has become quite clear and nearly colorless (the digestion should take from 4 to 5 hours).

After cooling, dilute with about 200 cc. of water. Next add 50 cc. soda solution, or sufficient to make the reaction strongly alkaline, pouring it down the side of the flask so that it does not mix at once with the acid solution. Connect the flask with the condenser, mix the contents by shaking, and distil until all ammonia has passed over into the standard acid. The first 150 cc. will generally contain all the ammonia. The operation usually requires from 40 minutes to 1½ hours. The distillate is then titrated with standard alkali.

Previous to use, the reagents should be tested by a blank experiment with sugar, which will partially reduce any nitrates present that otherwise might escape notice.

PROVISIONAL METHOD FOR SULPHONATED OILS.

MOISTURE.

Weigh between 30 and 40 grams (depending on amount of water present) into a flask of 250 to 300 cc. and add 75 cc. water

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saturated xylol, prepared by heating a mixture of water and xylol with frequent shaking and subsequently removing the water in a separatory funnel. Connect to a Liebig condenser and place flask in a bath of paraffine or a heavy lubricating oil. Distil moderately until the distillate comes clear. Collect distillate in a tube graduated to 1/10 cc. and wash condenser with a stream of xylol from a wash bottle. Place graduated tube in hot water and when the distillate is clear, cool. The percentage of moisture is obtained by dividing the volume of water in the distillate by the weight of oil taken.

NOTE.—For the graduated tube Eimer & Amend's No. 3812 is recommended.

ASH.

Weigh any convenient quantity into a dish or crucible. Ignite gently, allowing the oil to burn and complete incineration until all carbon is consumed.

NON-SAPONIFIABLE.

Weigh approximately 10 grams of oil into an 8-ounce Erlenmeyer flask and add 5 cc. aqueous KOH solution (50 grams KOH in water and dilute to 100 cc.), 45 cc. ethyl alcohol and a few glass beads. Boil 1 hour with reflux condenser. Add 100 cc. water and cool. Transfer to separatory funnel and shake at least three times with petrolic ether (B. P. 40° to 75° C.) using 50 cc. each time. Wash ether layer at least three times with 50 cc. water containing 10 cc. ethyl alcohol. Use alcohol to break emulsions. Evaporate ether extract in tared vessel, cool and weigh.

NOTE.—If the contents of the flask bump violently during saponification add 25 cc. petrolic ether, and proceed.

COMBINED SO_3.

(a) Weigh approximately 4 grams into an Erlenmeyer flask and boil for 40 minutes with 30 cc. HCl (1:5). Shake frequently. Cool, transfer to separatory funnel and shake out with petrolic ether. Draw off aqueous layer and wash ethereal layer with water. Combine washings with main aqueous portion and the sulphuric acid determine as barium sulphate. From the amount thus found, the quantity as determined in (b) is subtracted and the difference calculated as SO_3.

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(b) Dissolve 4 grams in ether and shake out several times with 25 cc. concentrated brine free from sulphates. Combine the washings, dilute, filter and determine the sulphuric acid as barium sulphate.

TOTAL FATTY OIL.

The total fatty oil shall be the difference between 100 per cent. and the sum of moisture, ash and non-saponifiable.

NOTE.—The results obtained by these methods shall be reported only in one decimal place.

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THE PURIFICATION OF TANNERY EFFLUENTS AND THE RECOVERY OF BY-PRODUCTS THEREFROM.*

By F. P. Veitch.

The problems involved in the purification of tannery effluents and the economical recovery of by-products therefrom do not lend themselves readily to co-operative investigations of the nature usually undertaken by this Association.

Since the proper handling of trade wastes and effluents is one of the several phases of sewage disposal, it has seemed the wisest policy in the beginning to bring together information on what has been accomplished in the broad field of sewage disposal; what processes and equipment can be relied on to give the best results; what is the approximate cost of installation; what legislative regulations must be met; what and how much of the by-products can be recovered and what use can be made of them.

To this end the knowledge gained in sewage disposal, as given in standard works on the subject, especially as it relates to tanning and other similar manufacturing wastes has been carefully studied.

Assistance has been sought from those tanneries and chemists directly interested, and the information so far obtained is presented with recommendations in this and the report for 1912.

The increasing realization of the importance of the subject is shown by legislation, by installations for purification, by the interest displayed by the industry in the subject, and by the fact that several papers on it will be presented at this meeting. It is not

*Read at the Eleventh Annual Meeting, *A. L. C. A.*, Chicago, Oct. 29, 1914.

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too much to hope that a large mass of very definite data, based on the disposal of tannery wastes alone, will soon be available to those who deal with the purification of tannery wastes.

Pollution of Water Courses Forbidden by Law.

Pollution of surface waters to such an extent that they become a menace to public health, or a nuisance, is forbidden by existing State and Municipal laws and regulations. The enforcement of these laws is usually assigned to the public health authorities supplemented by police assistance. As a rule these laws have been "more honored in the breach than in the observance," except in very thickly populated sections where the stench or physical condition of rivers and streams constitutes a public nuisance or where the public water supplies are seriously endangered or threatened by pollution.

The State laws relating to the pollution of natural waters are summarized, with quotations from the more important portions of the texts, in Bulletin 152 of the Water Supply and Irrigation Papers of the U. S. Geological Survey. No other publication summarizing later developments in sanitary laws has been issued, though it is possible that some of the States have enacted more stringent laws since it was issued.

Up to 1905, Connecticut, Massachusetts, New Hampshire, New Jersey, New York and Pennsylvania, had enacted severe restrictions on the pollution of natural waters. The principles of these laws may be summarized and stated in a few general rules, familiarity with which should be of service to tanners. Naturally, these rules are only general and many exigencies will arise in which more particular instructions must be sought, either of counsel or of the State authorities charged with the enforcement of the State sanitary laws.

Rights and Duties of Reparian Owners.

The Bulletin referred to above (pages 141-143) states:

"Every riparian owner has the right—

"1. To use the water of streams, navigable and otherwise, which flow across or along his property for the ordinary purposes incidental to domestic life and agriculture, including grazing.

"2. To use such waters for water power and for all kinds of

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manufacturing purposes which do not sensibly diminish the quantity which flows on for the use of the lower proprietors nor change the quality of the waters to any appreciable extent, nor interfere with the use of the stream, if navigable, by the public.

"3. To have such waters flow to him from the premises of higher proprietors not unreasonably diminished nor diverted nor rendered impure by the farming or domestic uses to which the waters are subjected by higher proprietors.

"4. To have such waters flow to him not sensibly changed in quality by any manufacturing or other uses to which they may have been put by higher proprietors.

"5. To have such waters flow to him in their natural bed, unpolluted by any deposit of filth or any other substance in the bed or channel previously traversed by them. But 3, 4 and 5 do not apply to riparian owners in these States in which the doctrine of prior appropriation is the law.

"Conversely it is the duty of every riparian owner—

"1. So to guard his use of the waters of streams which flow across or along his property for domestic and agricultural purposes as not to unreasonably divert nor to diminish nor to render impure such waters.

"2. To refrain from every use in manufacturing which will divert or sensibly diminish the quantity of the waters which flow onward to the lower proprietors or render them appreciably different in quality.

"3. To refrain from depositing any filth or other substance in the bed of such streams in such a manner or to such an extent as will cause the waters to flow to the lower proprietor out of their natural bed or will in any wise pollute or render them impure.

"Where the doctrine of prior appropriation is in force the appropriator must confine his use of the appropriated water to the use for which he has appropriated it and take only so much as is reasonable necessary to accomplish that purpose. He may not pollute the stream wantonly, nor by using it for purposes not included in his appropriation. Subject to these restrictions, the prior appropriator has the right to divert from the stream and use as much of the water as is necessary to accomplish the purpose for which it is appropriated."

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Municipal corporations have such rights and powers only as are conferred upon them by statute either expressly or by necessary implication, otherwise they have only such rights and duties as other riparian proprietors and must refrain from the pollution of streams the same as private owners.

The public, aside from the right to use navigable waters for commerce, has the right to enjoy the natural waters and the air which passes over them, so far as life and health are affected by these elements, in the condition in which nature left them, so that their use will not destroy nor threaten life nor injure health.

And, reciprocally, the public, and each member of it, is charged with the duty not to pollute the natural waters upon which the community depends for life and health in any manner that will render the continued use of the waters, or of the air which passes over them, destructive of or injurious to the life or health of the community.

There is a noticeable increase in recent years in public activities as to the prevention of pollution of drainage systems. This activity is indicated not only in the passage of the most stringent sanitary legislation, but by the greater activities of health authorities under existing laws. Further than this, courts have in general shown sympathy toward the protection of public rights in regard to pollution. In general, it may be said that the laws now upon the statute books are ample to prevent the serious pollution of drainage waters, used as public water supplies, and may be invoked by the State Board of Health, the Municipalities, Corporations or individuals.

It may therefore be anticipated that the requirements as to the prevention of pollution by tannery and other wastes will be, not only more stringent as time goes on, but will be enforced more vigorously than they have been in the past, and as stated in the report two years ago, the tanners especially must prepare themselves for the time when they will not be allowed to pollute the drainage areas of their community. To help meet the conditions which confront the industry, is the purpose of this Association in giving consideration to the subject.

The requirements of any State as to the prevention of pollution by trade and other wastes can as a rule be learned by communicat-

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ing with the State Board of Health or the State Sanitary Commission in the State where the plant is located, and often suggestions and other assistance can be secured from the State Boards of Health.

It will be seen from the foregoing that State or Municipal Officers have in most instances ample authority under existing legislation to prevent the serious pollution of natural waters, and where this authority has not been exercised vigorously it is probably due chiefly to the indifference of the public or to the lack of necessary appropriations and machinery therefor.

Purification Must be Effected by the Pollutor.

The question has often been asked, whose duty is it to prevent the pollution of surface waters. This question has been answered in the above statements concerning the rights and duties of ripairan owners. The person, corporation or municipality that is responsible for polluting material, must take the necessary steps to prevent its damaging effects to others. In certain cases where the manufacturing interests exercise a preponderating influence in a municipality, the purification of the manufacturing wastes is undertaken by the public in connection with the purification of ordinary household sewage. This has been done at Gloversville, N. Y., under municipal regulations which require the partial purification of trade wastes that they may not differ widely in composition from the normal household sewage handled by the sewage system of the city. Requirements of the same general nature are in force abroad, especially in England, where it seems the municipal authorities have the right to deny to any plant the privilege to empty wastes into the city sewage system.

Standards of Purity for Effluents.

Various standards of purity have from time to time been formulated in England, but in the United States no definite standard has been decided upon. The desirability of a standard of purity to which all sewage effluents should be made to conform, has aroused much controversy, the difficulty being that no account is taken in such standards of the nature or the volume of the water or the use that is made of the water into which the effluent is emptied. According to Kinnicutt, Winslow and Pratt, the usual require-

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ments in this country are that the effluent must be non-putrescible, or must contain only that amount of organic matter which when the effluent is emptied into the stream can be oxidized by the oxygen contained in the water at the time of minimum flow. The most important point therefore to be determined and to be considered in sewage effluents, is whether or not they are putrescible or whether they will improve or deteriorate when emptied into a given water course and whether or not they contain intestinal or typical sewage bacteria.

In general a sewage effluent is not putrescible when it contains sufficient oxygen either as free or combined oxygen in the form of nitrates for the complete oxidation of the nitrogenous organic matter and the sulphur compounds contained in it, though a complete statement should also take into account the carbohydrates and fat.

The Committee of the American Public Health Association in its 1911 report takes the position that it does not feel called upon to establish at the present time, any standards of purity, as these should be determined by the various administrative authorities interested in the subject. Fuller, on "Sewage Disposal" takes the position that the sanitary requirements, at least of the present day, do not require a uniform degree of the purification of sewage effluents, but that elimination of gross nuisances should be insisted upon and that further procedure should be along such lines and to yield such purity as each local community requires.

The Metropolitan Sewage Commission of New York recommends with special reference to the waters of New York Harbor, that no solid matter recognizable as of sewage origin shall be put into the water; that no marked discoloration or turbidity due to sewage or trade wastes, effervescence, oily sleek, odors or deposits shall occur, except perhaps in the immediate vicinity of sewer outfalls, and then only to such an extent and in such places as may be permitted by the authorities having jurisdiction over the sanitary conditions of the harbor; that the discharge of sewage shall not materially contribute to the formation of deposits injurious to navigation; that the dissolved oxygen in the water shall not fall below 3 cubic centimeters per liter; and that the quality of water at points suitable for bathing and oyster culture shall

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conform substantially in bacterial purity to drinking water standards.

Black and Phelps (*Mass. Inst. Tech. Quarterly*, 7, 189-93) state, with reference to the waters of New York Harbor, that 30 per cent. of the dissolved oxygen can be removed by sewage with safety, but that a greater loss than 50 per cent. will cause the water to become offensive. New York Harbor waters should be pure and should maintain major fish life everywhere. This requires that the dissolved oxygen shall be about 70 per cent. of saturation.

It may be pointed out that from a practical standpoint the permissible impurity in an effluent discharging into the surface waters is governed quite largely by the dilution which it undergoes when the stream is at its minimum flow, that is, an effluent which is acceptable to empty into a large stream, might not be permissible in a small one.

The above summary of the attitude of sanitarians in this country will serve as a guide to the tanner in reaching a conclusion as to the nature of an effluent which would be acceptable to the sanitary authorities of his State. But in all cases definite advice should be sought of the State sanitary authorities.

Volume of Effluent.

The figures given in the previous report presented at the annual meeting, December, 1912, were the subject of considerable comment and criticism by the members of the Association. It was stated that instead of an effluent of 100 gallons per day per hide, the figures given, the quantity was much larger, one tanner stating 300, another from 300 to 375, while a third gave as high as 500 gallons per day per hide.

Unquestionably the amount of effluent from tanneries varies widely, and undoubtedly the figures given by various members above noted, are substantially correct for their conditions. On the other hand, a much smaller volume of effluent is produced by others, especially by foreign tanners, many of whom do not run to waste materially more than 100 gallons per day per hide. The same statement has since been made to me by some American tanners who state that the figures given in the 1912 report fairly represented their conditions.

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The following figures on the character and distribution of the effluent, from a tannery handling in the neighborhood of 3,000 horse and calf hides per day are of interest; 4,000 gallons of spent soaks, 1,200 gallons of spent chrome liquor, 1,200 gallons of spent pickle, 1,000 gallons of spent bate, 7,650 gallons of sulphide sludge, 121,500 gallons of wash water, making a total of 136,550, of which about 15,000 gallons are, what may be termed highly impure wastes, the remainder being wash water which from the nature of its use can contain but little dissolved matter.

This matter of the volume of effluent is referred to merely to bring out the thought that in view of the fact that the regulations regarding harmful effluents will undoubtedly be more rigidly enforced in the future, making it necessary to purify effluents before running them to waste, it will probably be economy to make the volume of effluent as small as possible without detrimental effect upon the finished leather, and since it seems to be perfectly feasible to produce leather with but 100 gallons of waste per hide per day, other tanners using much larger quantities can probably do the same. It is quite evident that if a tanner can make leather with a waste of but 100 gallons per day per hide, that the expense of purifying this waste must be, in general terms, but a third of that of another with a waste of 300 gallons per day per hide. As a concrete example, the tannery producing 1,000,000 gallons of waste on a basis of 100 gallons per day per hide, would require a sprinkling filter of one-half an acre area, which would probably cost from $15,000 to $25,000 to install. Working on a basis of 300 gallons of waste per day per hide, a sprinkling filter of an area of an acre and a half would be required, which would cost from $45,000 to $75,000. In other words, the smaller the volume of effluent the less the cost of purification.

Preferred Methods of Purification.

Later data and recent developments concerning sewage purification, confirm in general the conclusion submitted in the previous report, though some amplifications of this report and possibly some modification of methods of treatment seem advisable.

In the first place, tannery effluents should always be subjected to sedimentation before filtering. This is absolutely necessary,

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as otherwise the amount of suspended matter would be too great to permit the proper handling of the effluent by the filters. In general, the lower the amount of suspended matter the larger the amount of effluent which can be put through the filter in a given time. In any case the amount of suspended matter should not exceed about 300 parts per million, and it would be preferable to have it much less. If the sewage contains more than 300 parts per million of suspended matter, it is almost certain that it cannot be properly purified by passing it through an acre sprinkling filter at the rate of 2,000,000 gallons per 24 hours. Furthermore, it is the settled sediment or sludge from the effluent which can be sold, and pay for or reduce the cost of purification.

In no case should the lime mud from the unhairing pits be mixed with the other effluents. The suspended lime should be settled and only the liquid portion mixed with the other waste liquors. If the lime mud is mixed with the effluent the volume of sludge is greatly increased and its fertilizer value materially reduced, because so large a quantity of inert material is mixed with the nitrogenous matter, the most valuable constituent of the settled sludge. Lime mud should always be kept separate from the other waste and sold or given away by itself.

Since the greater the proportion of material removed by sedimentation the easier it is to purify the effluents and the larger the quantity of salable material, it is possibly advisable and in fact often practiced in sewage disposal work, to add alum at a certain fixed rate, determined by experiments, to the effluent before it enters the settling tanks. This is for the purpose of precipitating much additional material which would remain in solution and tend to clog the trickling filter.

After settling, the supernatent liquid passes to the trickling filter while the sludge in the bottom of the settling tanks may be filtered through the ordinary filter press or through a leaf filter, the sludge dried in a rotating dryer, packed and sold to fetilizer dealers or farmers and the filtrate from the presses mixed with the liquid in the storage tanks from which the trickling filter is fed.

The efficiency of the trickling filter is intimately interrelated with the rate of flow and the depth of filter. In general the

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more impure the sewage the lower the rate of flow and the deeper the filter should be in order to obtain a satisfactory effluent. For the proper purification of tannery effluents in no case should the trickling filter be less than 6 feet deep nor the rate of flow more than 2,000,000 gallons per acre per 24 hours. Personally I am inclined to think, that it would be economy in the long run to make the trickling filters 9 feet deep and keep the rate of flow well under 2,000,000 gallons per acre per 24 hours.

The trickling filter must not be allowed to freeze in winter, and should not be worked beyond its capacity. If it is, the purification is far from complete and indeed in many cases even under the most favorable conditions the effluent from the trickling filter rarely complies with the health authority requirements and must be subjected to further sedimentation, since the effluent from the filter contains considerable quantities of sediment, usually about half a ton per 1,000,000 gallons. This material if run to the streams constantly, will clog and pollute them, the extent of pollution depending on the relative volume of effluent to stream flow.

The effluent from the trickling filter should therefore be further purified by sedimentation in settling tanks, filtering through spent bark, or better, through sand or by treatment with hypochlorite at the rate of from 5 to 10 parts of chlorine per 1,000,000. This latter treatment it is claimed will make the material comply with all reasonable requireemnts as to purity.

Sprinkling filters may give rise to objectionable odors especially when working on stale sewage, for this reason it is advisable to purify the sewage as soon as possible and to install the filter at some distance, 1/8 to 1/4 mile, from habitations.

Cost of Purification.

The figures for construction costs given in the previous report are probably as accurate as can be given. Naturally the cost of purification plants will vary considerably with local conditions and for other reasons. For convenience some of these figures are repeated here.

Total cost of purification plants, depending on construction and local conditions may vary from about $35,000 to $75,000 for 1,000,000 gallons per 24 hours.

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TABLE I.—Approximate Area, Cost and Capacity of Works for Treating 1,000,000 Gallons of Sewage per 24 Hours.

	Area	Capacity gals.	Cost
Settling tanks	3,000 sq. ft.	150,000 to 200,000	$8,000 to $15,000
Filter presses for sludge			$1,000
Rotary dryers			$2,300 to $3,000
Sprinkling filters (9 feet)	½ acre		$22,000 to $37,000
Final settling tanks	1,000 to 2,000 sq. ft.	75,000 to 100,000	$5,000 to $10,000
Hypochlorite treatment	400 sq. ft.		$1,000

Other costs and capacities may be obtained from these figures proportionately.

The construction work is simple and with proper plans and specifications, prepared by an experienced and competent engineer, intelligent workmen can build the works under the immediate supervision of the tannery staff.

The cost of operating sewage works varies considerably. At some works it is stated to be as low as $5.00 per 1,000,000 gallons of sewage treated, at others it runs as high as $9.00. In these figures, depreciation or maintenance and interest on investment are not included. On the other hand rather high charges for supervision, analytical and clerical assistance are included, and it is probable that the cost of operation for privately owned works is no greater than is indicated by the above figures.

The following table compiled from the various authorities on sewage disposal contains information and data of value on the cost of certain operations.

If the pressed sludge containing 70-75 per cent. moisture is dried in rotary dryers from $1.25 to $2.00 should be added, and if the dried sludge is bagged, $1.00 to $2.00 should be added, bringing the total cost up to from $8.00 to $13.78 per 1,000,000 gallons of sewage. From this should be subtracted the value of the bagged dried sewage, varying from about $3.00 to $10.00, making the net

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cost for purification from about $5.00 to $10.75 per 1,000,000 gallons.

TABLE II.—Data on Sewage Treatment.

Lime used, per 1,000,000 gals.	485 to 990 lbs.
Copperas used per 1,000,000 gals.	65 lbs.
Organic matter removed, total (by albumoid ammonia)	34.9 to 51.77%
Organic matter removed, suspended (album. ammonia)	77.8 to 91.6 %
Wet sludge (percentage of total sewage flow)	0.445 to 0.478%
Wet sludge, average dry solids, tons per 1,000,000 gals.	5.37 to 7.93
Pressed sludge, percentage dry solids	27.6 to 30.3 %
Pressed sludge, tons per 1,000,000 gals.	3.7 to 5.6
Dry solids in sludge, tons per 1,000,000 gals.	1.07 to 1.45
Cost of sludge pressing and disposal, per ton dry solids	$2.27 to $3.39
Cost of sludge pressing and disposal, per 1,000,000 gals. sewage	$2.44 to $4.63
Total cost of treatment, per 1,000,000 gals. sewage	$5.75 to $9.78

These figures are for mixed domestic and manufacturing sewage and are not strictly applicable to tannery effluents, but it may be safely said that it should be possible to bring the cost for these well within these figures, and at the same time turn out an effluent that will meet sanitary requirements.

Suggestions for Procedure and Equipment for the Purification of Tannery Effluents.

After a careful general study of the work which has been done in sewage purification and the recovery of trade wastes, the following suggestions are offered for the handling of tannery effluents.

The volume of effluent should be as small as possible without injuriously affecting the main product, leather. This object may be accomplished by the repeated use of various solutions, of wash and rinsing waters, the object being to have each waste liquid that flows from the tannery as concentrated as it is possible to make it, and at the same time maintain the proper working of the various tanning processes and the high quality of the leather.

When the installation of sewage disposal work is contemplated, a careful study of the relative volumes of waste from the several tanning operations should be made, together with a determination of the amount of total solids, of volatile and non-volatile solids, of nitrogen, lime and possibly chromium and arsenic in the liquid.

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Especially should each of the foretanning wastes and the waste tan-yard liquors be carefully examined, both as to volume and contents of the above mentioned constituents. The wash and rinse waters should be examined, as well as the other effluents, with the view to their repeated use and to the probability of running such liquids direct to the sewer without purification. It is altogether possible, if not probable, that the rinse and wash waters and the bleach solutions used on the finished leather are practically harmless bacterially, and contain but little putrescible material. The main objection to them would be the presence of a considerable amount of tanning material washed out of the leather. The lagooning of these liquids would probably be all that is required in any case. This examination of the waste liquors from the tannery will show whether or not any of them can be used more frequently than they are now and give definite information as to the total volume and composition of the effluent which must be purified.

The waste limes should be settled, the supernatant liquid being mixed with the main effluent to be filtered, while the sediment consisting of carbonate of lime and sand should be drained, spread out to dry as much as possible, and given to the farmers.

The mixed effluent, other than that from the limes, should be run to settling tanks of the Imhoff type, which various engineers have found to give the most satisfactory results with trade effluents, or to tanks with conical bottoms. The Fullner filter used in the paper industry, for the recovery of waste fibers will probably serve. As the effluent passes to the settling tanks it should have added to it a sufficient quantity of aluminum sulphate or copperas solution to precipitate the maximum amount of solids. This is advisable because the more suspended and dissolved mattter that can be removed from the effluent by preliminary treatment, the more readily it can be subsequently purified, and the smaller the trickling filters need be. Moreover a slightly acid effluent filters more rapidly.

After remaining in the settling tanks a sufficient period to insure sedimentation, the supernatant liquid should pass to storage tanks so situated that the liquid will flow to the sprinkling filter under

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sufficient head or pressure, (12 to 15 feet) to insure the proper distribution through the sprinklers.

The wet sludge from the sedimentation tank should be filter-pressed either with the ordinary leaf or section filter or be centrifuged, to reduce the moisture in it to approximately 70 per cent. This sludge should then pass to a rotary steam dryer where it is dried to about 10 per cent. moisture, thus making what may be termed "sewage tankage," which should be worth for fertilizer purposes, from $3.00 to $8.00 or $10.00 per ton, depending upon the amount of nitrogen and organic matter which it contains. The market for this sewage tankage should be either the farmers of the immediate locality, or dealers in fertilizer materials. The latter are located in all of the large cities. It may be well to sell direct to the fertilizer manufacturers, many of whom are in business in each State. The names and addresses of these can be had from the American Fertilizer Handbook, published by Ware Bros., Philadelphia, Pa.

The sprinkling filter, in my judgment, should be 9 feet deep for proper purification, and should not be operated at a greater rate than 2,000,000 gallons per acre per 24 hours, when the effluent passing to it contains approximately 300 parts per 1,000,000 of suspended solids. Should the sewage contain more than 300 parts per 1,000,000, the rate should be slower, if it contains less, the rate may be faster. The depth of the filter and the rate of flow are closely inter-related, and it is probable that with shallower trickling filters further purification through sand filters, or by hypochlorite treatment, will be required to insure acceptable purification.

The effluent from the trickling filter contains suspended solids which if the effluent were run immediately to the streams and rivers would cause decidedly objectionable deposits. It is therefore always advisable to provide a final sedimentation tank of sufficient size to permit the settling of the suspended solids from the trickling filter effluent. When this is accomplished, the supernatant liquid may be passed directly to the water courses the wet sludge filter-pressed, the liquid going to the water courses and the pressed sludge is mixed and dried with other sludge.

The effluent from the final sedimentation tanks should be tested

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from time to time to determine its compliance with reasonable sanitary requirements and should it be found that the effluent does not meet these requirements, the necessary steps should be taken to make it do so.

The installation of works for the purification of tannery effluents is not a very difficult and complicated problem. After the data as to the volume and composition of the effluent has been obtained experienced engineers can prepare the necessary plans and specifications, and labor of ordinary intelligence under the supervision of the management of the tannery should be able to erect and install all of the necessary appliances.

Disposal of Wastes.

Many of the waste products of the leather industry are now regularly disposed of by practically all tanners. Among such wastes are, spent bark, hide cuttings, trimmings, hair, and in a very limited way, waste lime. Scrap leather, leather shavings, etc., are to a certain extent being disposed of economically, the material bringing, when uncurried, in the neighborhood of from $3.00 to $5.00 per ton, while if curried the price rises to as much as $9.00 to 10.00 per ton.

It is the waste liquors of all kinds and the materials which they contain for which, as a rule, no really suitable way for disposal has been adopted.

The sludge obtained by settling, precipitating or filtering tannery wastes, as stated in the previous report, and sewage generally is disposed of in several ways, such as, burying in the ground, filling waste places or dumping at sea. None of these methods of disposing are to be recommended, since all of them are more or less expensive and unsanitary. It is believed that this sludge can be economically dried and sold to fertilizer makers, if not at a profit, at least for sufficient amount to cover the expense of drying and handling. Any dried sludge containing as much as 3 per cent. of nitrogen, and 80 per cent. or more organic matter, is salable to dealers in fertilizer materials. It may be that in certain localities a market will have to be established for the material. When there is very little material or an irregular supply of it there is practically no market, but when it is obtainable either in

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considerable quantities or with regularity, a market is sure to be established. That is to say, that while possibly one tanner would find more or less difficulty in disposing of dried sludge to fertilizer dealers, when there are a number of tanners producing it thus insuring a constant supply, the possibilities of selling it are increased.

ANALYSES OF DRIED TANNERY WASTES.

		Ash per cent.	Nitrogen per cent.	Phosphoric acid per cent.	Lime per cent.	Fats per cent.	Chromium oxid per cent.
24851	Waste from settling tanks	31.3	2.2	0.3	10.6	2.4	0.3
24854	Fleshings out of soaks	5.5	11.2	0.5	1.1	5.9	—
24853	Sludge from beamhouse	56.9	1.9	—	23.8	0.9	—
24852	Sludge from soaks, bate and color room	35.1	6.9	—	1.0	2.8	—
29300	Sludge from sulphide process	14.7	8.5	0.2	0.4	—	0.26 As_2O_3
29968	Sulphide waste	14.6	8.4	3.0	0.3	—	trace
27588	Tannery waste	86.2	1.2	0.7	29.4	0.3	1.43
24951	Tannery waste	25.4	2.6	—	8.4	5.5	0.78 Cr_2O_3
24950	Tannery waste	45.6	3.1	1.2	9.5	2.9	2.2
24949	Tannery waste	66.7	1.1	—	6.9	6.5	—
24948	Tannery waste	39.3	1.9	0.67	8.9	10.2	0.11
24947	Tannery waste, alum precipitate	33.7	2.1	0.85	9.9	13.5	0.22
24946	Tannery waste, natural sedimentation	47.9	1.5	none	10.1	13.1	0.89
24855	Settling basin waste dried	58.5	1.8	0.3	26.1	1.2	0.35
24812	Sludge beamhouse settling tanks	37.7	5.3	0.1	24.8	1.9	—
24811	Sludge beamhouse settling tanks	63.5	0.8	—	11.6	1.5	—
24688	Sludge from mixed liquors	42.0	0.9	0.8	27.5	0.4	—
20405	Tannery waste settling tanks	43.9	3.0	0.7	15.3	1.9	—
25544	Tannery waste settling tanks	24.6	2.8	—	8.1	—	—
25543	Tannery waste	48.4	2.4	1.0	8.4	1.9	0.64 As_2O_3
25181	Mainly lime, arsenic and sulphide of sodium and short hair	62.5	2.0	0.3	33.9	1.2	6.92
26756	Wash liquor from lime pits	62.6	0.8	0.1	55.0	0.1	—
20404	Tannery waste settling pools	33.0	4.3	0.8	16.0	0.3	—
27352	Tannery waste first pools	72.2	0.9	0.2	11.0	0.6	—
27351	Tannery waste Imhoff tank	23.9	4.4	0.36	9.2	1.8	—

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The dried sludges obtained from tannery effluents vary considerably in composition, as shown in the table of analysis of the dried wastes on p. 141. The wet materials, in the form of sludge from the filter presses or centrifugals, contain from 50 to 75 per cent. of water.

From this table it is seen that dried wastes now differ widely in composition, containing:

	Per cent.
Nitrogen from	0.8 to 8.0
Phosphoric acid	0.0 to 0.8
Volatile matter (organic matter, moisture and carbon dioxide)	20.0 to 85.0
Ash	14.0 to 60.0
Lime	0.5 to 35.0
Fats	0.0 to 14.0
Chromium oxide	0.0 to 1.0
Arsenic	0.0 to 7.0

The value of this dried sludge may be increased though the quantity is diminished, by keeping the waste lime separate from the other wastes. From a fertilizer standpoint, free lime is an undesirable constituent, since it interferes more or less with the solubility of the phosphoric acid in the fertilizer to which the sludge is added. If the waste lime is kept out of the sludge, the percentage of organic matter and of nitrogen would be correspondingly increased, and in many instances the nitrogen would be practically doubled. This would not be true probably of those dried sludges which contain 6 to 8 per cent. of nitrogen but would be true as a rule of those that contain from 1 to 3 per cent. These could be made to contain from 2 to 6 per cent., by keeping the waste lime out of them.

The fertilizer value of dried sludge is determined almost entirely by the nitrogen and phosphoric acid which the material contains. Sludges containing little free lime should bring, if regularly obtainable and in considerable quantities, about the same price proportionately as garbage tankage, which contains 3 to 6 per cent. of nitrogen and sells at from $6.00 to $10.00 per ton. On this basis, what may be called "sewage tankage," containing 2 per cent. should sell for about $4.00 to $6.00 per ton, while sewage tankage containing 6 per cent. of nitrogen should sell for about $10.00 per ton

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A warning should be given regarding the presence of dangerous or undesirable constituents In view of the very poisonous nature of arsenic, care should be taken in disposing of sewage or sludge containing a considerable quantity of the substance. No statement can be made at this time as to the permissible amount of arsenic allowable in dried sludge. A large amount of grease in the material interferes with its value as a fertilizer, and should the grease exceed 10 per cent., it should be extracted. Usually this can be done profitably, since a fairly ready market exists for it.

While it is not anticipated, as stated in the previous report, that sludge and lime can be made profitable, it seems reasonably certain that these materials can be disposed of in a sanitary way at no expense to the tanner.

The waste lime can best be disposed of by giving it to the farmers of the surrounding country, if they will haul it away. It will hardly pay to dry and grind waste lime, to put it to the mechanical condition that will warrant the farmer in purchasing it, since lime, either the ground limestone or the burnt lime, is so cheap. It should be spread out however, to permit it to dry as much as possible under natural conditions.

The likelihood is, that since the importance of lime in agriculture is being more and more realized, both by the farmers and Experiment Station workers, that no great difficulty will be encountered in thus disposing of the waste lime. Especially is this true, if the tannery will make some effort to interest the farmer in the matter, such as publishing a statement in the local paper that the lime will be given for the hauling away. It would also be worth while to notify the State Experiment Stations that the lime will be given to the farmers. These stations constantly receive requests for information, both on the use of lime and where it may be obtained. The stations will always be glad to co-operate with the tanners in helping them to dispose of their lime and other waste products of farm value in this way.

Undoubtedly, a considerable amount of undried sludge could be disposed of to the farmers through these same channels. One of the great reasons for the apparent indifference of farmers to

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the value of tannery wastes, is the fact that their attention has not been properly directed to the materials.

Many farmers make a practice of hauling manure from the cities, paying 50 cents for a two horse load, of material which contains about 50 per cent. of moisture. It is believed that no difficulty whatever would be encountered in disposing of sludge if some effort is made to inform the farmers generally of its availability, and of the fact that it can be had for the hauling away.

AN APPARATUS FOR STUDYING THE MELTING POINT OF PARAFFIN WAXES.

By F. H. Small.

Commercial paraffin wax is not a chemical individual but is a mixture of related compounds. It has no melting point in the strict sense of the term, its so-called melting point being merely the average of the melting points of the numerous waxes making up the composite whole. Two samples of paraffin wax, designated as of the same melting point, may be of radically different composition; one for instance, a so-called crude, may consist of individual waxes whose melting points cover a wide range of temperatures, while the other, a refined wax, may consist to the extent of over 90 per cent. of waxes whose melting points lie within a range of 5 degrees. Naturally these two waxes will not behave in the same way, will not show the same plasticity and physical qualities, even though they be labeled with the same melting point. It was to secure a more definite idea of the composition of a commercial paraffin wax than was afforded by a simple melting point determination that the apparatus described below was constructed.

The apparatus and method are somewhat crude but have been found sufficiently accurate for commercial purposes. The several parts of the apparatus are shown in the accompanying diagram:

"A" is a glass tube, the smaller part being of uniform bore and graduated in equal divisions; "B" is a glass plunger the disk of which fits easily the bore of the enlarged part of "A." "C" is a brass disk bored to fit the stem of B and of the same external diameter as the disk of B. In use "B" is inserted in the upper

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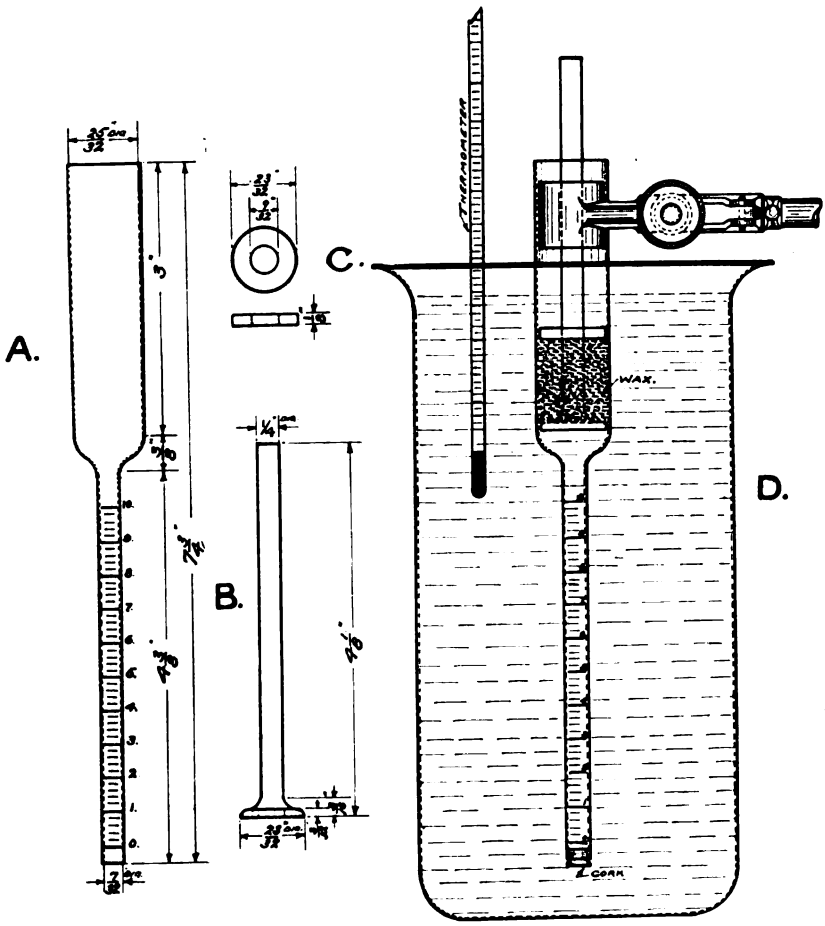
part of "A." Enough of the wax is shaved and introduced into "A" so that when melted it will nearly fill the graduated tube of "A." The brass disk "C" is then slipped on "B" and allowed to press down the shaved wax. The lower end of the graduated



tube of "A" is closed with a cork reaching just to the zero mark and the apparatus as prepared is inserted in a tall one liter beaker filled with water to above the level of the wax. See "D." The water is warmed by a burner below and is stirred at frequent intervals. The warming process is continued until such time as

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the wax shows signs of softening. The temperature is then raised very gradually, the plunger "B" being moved slightly up and down to facilitate the flow of any melted wax into the graduated tube. When some of the wax melts and runs down, the temperature at which this occurs is recorded. The temperature is now raised a degree at a time, being held at each degree 7 minutes, the plunger "B" being moved slightly up and down at intervals as before, to help free the melted wax. At the end of each 7 minutes the temperature and the scale reading are recorded. The process is continued until the wax is all melted. Since each scale division represents an equal part, a simple calculation shows the percentage of the wax melted at any given temperature. The temperature at which 50 per cent. was melted corresponds to the melting point as usually determined.

The accompanying table shows the information given by the method with regard to the two samples of wax studied by last year's Committee on "Hard Greases," and also the data obtained with regard to a crude scale wax. If the melted wax is allowed to harden in the tube an inspection of this core will usually show whether the wax contains any appreciable amount of oil.

	Sample "A"		Sample "B"		Sample "C"	
Temperature, °C.	Scale reading	Per cent. melted	Scale reading	Per cent. melted	Scale reading	Per cent. melted
45	0.00	—	0.00	—	0.00	—
46	0.00	—	0.00	—	0.38	4.6
47	0.00	—	2.14	25.5	0.95	11.5
48	0.00	—	3.98	47.5	1.97	23.8
49	0.00	—	5.13	61.2	2.98	36.1
50	0.04	0.5	5.90	70.4	3.85	46.6
51	0.73	9.1	6.52	77.8	4.99	60.4
52	1.73	21.6	7.40	88.4	5.80	70.3
53	3.74	46.9	7.81	93.2	6.58	79.7
54	5.34	66.8	7.89	94.2	7.20	87.2
55	6.16	77.0	8.00	95.5	7.66	92.8
56	6.76	84.6	8.11	96.9	7.80	94.5
57	7.25	90.7	8.20	97.9	7.96	96.3
58	7.54	94.3	8.26	98.6	8.12	98.4
59	7.71	96.5	8.30	99.1	8.17	99.0
60	7.81	97.7	8.32	99.4	8.19	99.2
65	7.99	100.0	8.37	100.0	8.25	100.0
Av. melting point		53.1		48.3		50.2

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NOTE ON THE TANNINS OF VALONIA, OAK-WOOD, AND CHESTNUT-WOOD.*

By Hugh Garner Bennett, M. Sc.

For some time the author has been engaged in an investigation for distinguishing better the various tanning materials, more especially those of the "pyrogallol group." The various tests suggested have each been confirmatory of the classification first proposed, *viz.*, that valonia, oak-wood, and chestnut tannins form one closely allied section, whilst sumac, myrobalans, and algarobilla fall into another section together. This arrangement is suggested by the following tests previously devised by the author, *viz.*, the chromate test, the iodine test, the aqueous ferricyanide test, the ammoniacal ferricyanide test and the ammonium cobaltate test. This arrangement is also in harmony with other tests devised by Procter and other workers, *viz.*, the lime water test, the sodium sulphite test, the copper sulphate and ammonia test, the lead acetate test, and the lead acetate and acetic acid test.

These two sections are now fairly sharply marked and can easily be distinguished. There remains the important problem of distinguishing the different individual members of each section. To solve this in connection with the valonia section is the object of this investigation. So far as the author is aware, the behavior of valonia, oak-wood, and chestnut tannins is practically the same towards every known test. The only slight differences are:— (1) In the lead acetate and acetic acid test, the precipitation of the tannin is complete with valonia and oak-wood and *almost* complete with chestnut. (The sumac section and mixed tannins give partial precipitation and catechol tans no precipitation.) (2) In the formaldehyde test valonia gives a slight turbidity, whilst the other two remain clear.

These differences are too slight to be of great practical value, and it is clear that some new methods must be devised. That there is actually a difference between these three materials is evident from the fact that valonia makes a different leather from chestnut, whilst oak-wood may be considered to be intermediate between valonia and chestnut in its practical effect.

The author has found that it is possible to distinguish these

* *J. S. C. I.*, Dec., 1914.

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three materials easily by the action of bromine water upon a solution of the products obtained when solid extracts of these materials are subjected to dry distillation. The extracts are evaporated to dryness on the steam bath, powdered, and dried further at about 30° C. if convenient. For the dry distillation an inexpensive retort is easily made from a piece of tubing about 6 inches long and rather over ½ inch in internal diameter, closed at one end, which receives a layer of the dried extract. The open end of the tube is fitted with a cork through which passes a delivery tube leading into a test-tube acting as the receiver. This delivery tube acts as an air condenser. It is best to keep the wide tube horizontal and to bend the delivery tube at right angles. The extract is gradually heated until blackened and is then strongly heated till no more distillate is received. This only takes 5-10 minutes. The distillate is shaken with 10-15 cc. distilled water and filtered from the tarry matters which remain undissolved. An excess of fairly strong bromine water is added to the filtrate and the mixture is shaken up well.

Under this treatment valonia yields a dense yellow crystalline precipitate, which after filtering, washing with cold water and drying, appears under the microscope as a mass of yellow plates. This precipitate has been found to be tetrabromophenol ($C_6H_2Br_3.OBr$) and exhibits the following properties:—It is insoluble in water and cold alcohol, and is best purified by washing with these reagents successively. The melting point of the crude substance varies according to the conditions of precipitation, but is generally between 120° C. and 136° C. After purification by washing repeatedly with cold alcohol it melts fairly sharply at 139°-141° C. with decomposition, bromine being evolved. Watts' "Dictionary of Chemistry" gives the m. pt. of these substances as 118° C., which led the author to think at first that the product he had obtained was an impure tribromophloroglucinol, $C_6Br_3(OH)_3$, m. pt. 151 degrees. An experiment with pure phenol, however, showed that the 118° C. was an error, and that tetrabromphenol, $C_6H_2Br_3(OBr)$, melts at 139°-141° C. like the product obtained from valonia. This product liberates iodine from potassium iodide, a reaction which appears typical of compounds containing the radicle—OBr. It cannot be recrystallized from alco-

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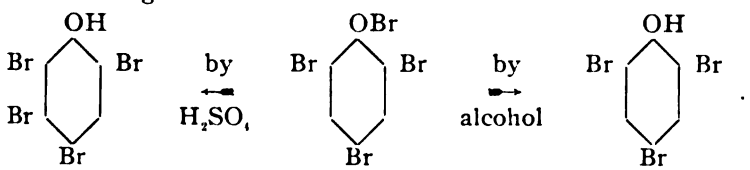
hol, as hot alcohol decomposes it fairly easily, yielding tribromphenol, $C_6H_2Br_3(OH)$. From very dilute alcohol this may be crystallized easily, yielding a felted mass of white needles, which after repeated recrystallization from dilute alcohol, give a melting point of 92° C. The product is also acted upon by warm sulphuric acid, undergoing intra-molecular change into its isomer tetrabromphenol, $C_6HBr_4(OH)$, which on recrystallization from dilute alcohol yields white needles with a m. pt. of 120° C.

These changes are indicated thus:—



mp 120° C. mp 141° C. mp 92° C.

Under similar treatment the tannin of chestnut yields no precipitate with bromine water and hence none of the above products. The two materials are thus very easily distinguished, and there seems little doubt that this difference involves a radical difference in the constitution of the respective tannin molecules. It is clear also that it would be an easy matter to detect the presence of valonia tannin in mixture with chestnut or any other tannin which under this treatment yields no precipitate with bromine water.

Under this treatment the tannin of oakwood yields a distinct turbidity with bromine water, but in the author's first experiments he failed to filter this precipitate for purposes of investigation. Repeated attempts, however, and larger quantities yielded a small quantity of a dark product melting at 107°-112° C. This dissolves in hot alcohol, which upon dilution and cooling yielded white felted needles, m. pt. 86°-89° C. There can be little doubt that these are the same products (only impure) as were obtained in the case of valonia, but the quantities obtained were so exceedingly small that further purification and investigation were impossible. This indicates that oak-wood also contains at any rate a small quantity of that tannin which yields phenol on dry distillation. This behavior justifies the statement made above that the practical effects of oak-wood are between those of valonia and chestnut.

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Under a similar treatment myrobalans behaves like chestnut, and yields no precipitate with bromine water. This gives some chemical justification to the tanner, who, when he desires to substitute "extract" in his tannage for "dry material," uses oakwood to replace valonia, and chestnut to replace myrobalans.

This distillation process has been repeated a good many times with each of the materials mentioned, and that there is little doubt that the result is the characteristic behavior of each of the materials in question. The results, moreover, are somewhat encouraging to the view that in this way it is possible not only to differentiate the different tannins, but also to throw some light upon their chemical constitution. The work is being continued with the tannins of other groups, upon which it is hoped to report later. The results, so far, indicate that the other members of the pyrogallol group of tannins (myrobalans, gallotannic acid, etc.) yield no precipitate with bromine water; whereas the catechol tannins (quebracho, gambier, mimosa bark, etc.) yield a precipitate which is *not* tetrabromphenol, but a sticky, tarry product which the author has failed to crystallize or purify.

Another line upon which it is hoped to obtain fruitful results is to apply other reactions to the products of dry distillation. The distillates from valonia, oakwood and chestnut, for example, give a precipitate with lead acetate, which may be due either to pyrogallol or catechol. They also give *feebly* the potassium cyanide reaction and the iodine reaction for pyrogallol. As these last are very delicate reactions there seems no doubt that pyrogallol is a minor product in the distillation; and it becomes a question whether valonia, oakwood, and chestnut can really be regarded as pyrogallol tannins, for neither their infusions nor their dry distillates give the reactions which are peculiar to the pyrogallol grouping. The exception is the purple color obtained with copper sulphate and ammonia precipitate. This is given by pyrogallol itself but is not given by the other pyrogallol tannins. The alternative conclusion, therefore, which is perhaps more probable—is that these three tannins are actually pyrogallol derivatives but that the pyrogallol grouping has a different place in the molecule, or a different relation to the rest of the molecule, than is the case with the other pyrogallol tannins.

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THE PROCTER INTERNATIONAL RESEARCH LABORATORY.*

The establishment of the Procter International Institute having become an accomplished fact, the members of the leather trade throughout the world will be interested to have some particulars of the work which it is proposed to carry out and on which a beginning has already been made. The opening of this laboratory will probably mark a new era in the scheme of advanced technical instruction as directly applied to a particular industry, for the possibilities of development in this direction are enormous. As far as we know, it is the only public building devoted entirely to advanced and specialized research work; in any case it stands as a unique institute in the leather trade.

A few particulars of its origin may be interesting. It will be remembered that Professor Procter, whose fame in the leather trade is of an international character, reached the age last year when, in compliance with the rules of Leeds University, he could no longer continue to hold his position as the director of the leather department. All will agree who have followed his work for years past that he had performed splendid service for the trade, and that he was fully entitled to rest from his arduous labors, but some of his friends, recognizing that his retirement would be a great loss to the trade, especially as he was engaged in some very important investigations at the time, suggested that a testimonial should be conferred upon him. The idea originated with Mr. Alfred Seymour-Jones soon after the conference of the I. A. L. T. C., held in Brussels some years ago, but it was not until the following conference that he mentioned it to several of the members, all of whom agreed that a tribute should be paid to the professor. A few years later the idea of a public subscription and presentation was mooted, but somehow or other the professor got to hear of the scheme, explained that he was not in want of money, and that, if anything were done in the matter, the amount should be devoted to the establishment of a research laboratory. Afterwards, to the great delight of his admirers, the professor not only agreed to continue his researches if it were possible to establish the laboratory, but also to act as

* *Leather Trades' Review*, Dec. 16, 1914.

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director in an honorary capacity. When it is duly considered that his services would command a very large salary in a private tannery, the extent of his personal sacrifice for the development of the leather industry can be fully gauged. That a professor, at the zenith of his intellectual power, and in the midst of the most difficult researches in the chemistry of the leather trade, should willingly give his services without payment is almost, if not quite, without parallel in the annals of science.

His consent given, a few of his friends broached the subject to the late Mr. W. J. Rivington, proprietor of the *Leather Trades' Review*, who not only undertook to make the first public announcement of the scheme (*L. T. R.*, September 18th, 1912, page 667), but also devoted considerable time and energy in carrying out the mass of detail which the scheme involved, until its success was assured. On the day following the announcement of the scheme, Dr. J. Gordon Parker, as President of the I. A. L. T. C., referred to the proposal at the International Conference of the Association, then sitting in London. He stated that a project was being formulated by which a laboratory might be provided and equipped, which would be international in its aims and character, and that it was intended that the building should be used for gratuitous research work connected with the leather industry. The members of the I. A. L. T. C. generously voted a sum of £100 towards the scheme, and Dr. Parker and Professor Meunier (France) were appointed to represent the association on the Procter International Committee then in process of formation. In the following October a preliminary advisory committee was formed, and a meeting took place in London, when the scheme took definite shape. The committee, which was of an international character, included some of the best-known practical and scientific men in the trade. (Here follows the long list of names.)

Of these gentlemen, Mr. M. E. Sadler, Dr. J. Gordon Parker, Hon. F. S. Jackson, Mr. Alfred Seymour-Jones, and Mr. W. J. Rivington were appointed as the Executive Committee. Later, national committees were formed in America, Austria, Belgium, France, Germany and Italy.

On January 29th, the British Advisory Committee issued their

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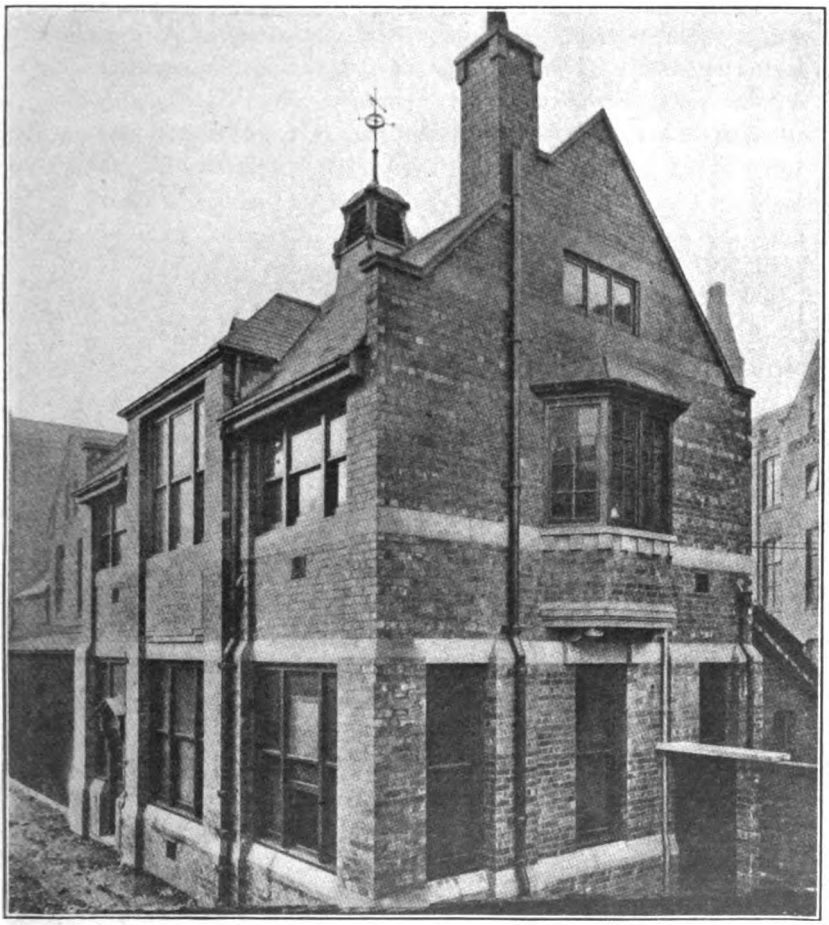
appeal to the trade for subscriptions, and a copy of this circular, together with a plan of the proposed laboratory, was published in the *L. T. R.* of that date. A review of Professor Procter's work in the leather trade, published in the circular, contains the



THE PROCTER INTERNATIONAL RESEARCH LABORATORY.

following paragraph, which is worthy of reproduction in view of the honor which it was decided to confer on him:—

"The great scientific services rendered to the leather industries by Professor Procter are well known to those who are familiar

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with the scientific side of the industry. He has worked out analytical methods for the estimations of all materials necessary for leather making. He has investigated and explained the principles of the different processes in leather manufacture. He has invented scientific methods for the control of a modern leather works. He has published the results of his investigations in a series of more than sixty papers, and has collected these results, together with the outcome of his personal experience, in the form of books which are recognized all over the world as of standard value. For more than 20 years he has devoted himself to teaching in the University of Leeds, and a large body of students are applying to the benefit of the leather industry the knowledge gained from him and from their studies in his care. In 1912 the Worshipful Company of Leather sellers conferred upon him the Honorary Freedom and Livery of the Company, and the International Association of Leather Trades, Chemists elected him as their permanent Hon. President at their Conference in the same year."

Mr. Rivington's appeal met with a generous response from the trade, and as is now well known, the total amount given, although not so large as was necessary to meet fully every expense, was yet sufficient to begin building operations, thanks to the gift of a free site by the Council of Leeds University. Donations were received from nearly all parts of the world, and the total amount collected was nearly £1,700, while, in addition, several annual subscriptions were promised.

Thus the leather industry is enabled to honor the greatest of its chemists during his lifetime, for, while Professor Procter is not the actual pioneer of leather trades chemistry, he is universally acknowledged to have placed science, as applied to our trade, on a practical and sound basis, on which a magnificent superstructure is now being built.

The Procter International Research Laboratory is semi-detached, being adjacent on one side to the Leather Industries Department of Leeds University, with which it communicates by doors both on the ground and first floor, the latter being in connection with one of the private laboratories which is not open to students. At the north end it faces a large open space, and

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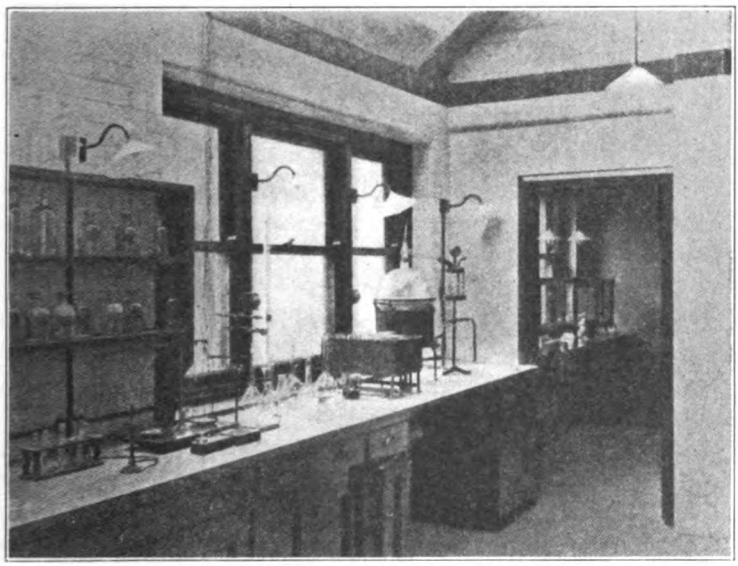
though its main front to the east is at present on a back lane, it is intended ultimately that this should be thrown into an open quadrangle. On the ground floor there is a laboratory intended principally for furnace work, and provided with a stone bench with the necessary gas, water and steam connections. On the upper floor is a larger laboratory for the use of research chemists, a balance room, and the directors' private room, which is also fitted with a small working bench. The laboratories are fitted with every convenience for scientific work, and lined with white tiles, while the fittings are of selected pitch pine, so that though



THE PROCTER INTERNATIONAL RESEARCH INSTITUTE (Part of Laboratory.)

perhaps somewhat expensive for its size, it is commodious, and splendidly adapted for its purpose.

The ideal of acquiring a special site and constructing the institute away from any other building was, unfortunately, unattainable, as the amount required for that purpose would have been at least £10,000. There is the possibility, however, that the principles underlying the work that will be carried on in the laboratory will be of such importance as to necessitate much greater facil-

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ities for research, in which case it may be decided to build a large institute which would continue to bear the same name.

Although the laboratory was unfinished at the beginning of the university autumn term, and, indeed, is not yet quite complete, no time has been lost in starting research work of a character which we feel certain will definitely determine the phenomena of the process of tanning.

With the approval of the Advisory Committee *pro tem.*, the Council of the University has appointed Mr. Donald Burton, B. Sc,. as assistant to Professor Procter, and, notwithstanding the fact that the latter has been compelled temporarily to resume the control of the Leather Industries Department of the University in addition to voluntarily undertaking the directorship of the Research Institute, a considerable amount of useful work has already been accomplished (partly in a temporary laboratory lent by the University) in relation to the swelling of hides and other proteids with acids, and a complete mathematical explanation in accord with the latest views of physical chemistry has been worked out, of which a part has already been published, while a second paper is almost complete. Briefly, the work shows that an actual chemical combination is formed between the acid and the hide-fiber (or the almost identical gelatine), and from the figures obtained both the molecular weight and the rational chemical formula for gelatine and indirectly for hide-fiber can be deduced. The whole phenomenon of swelling is shown to be merely a consequence of this constitution and of ordinary chemical laws, and with regard to gelatine at least, its amount for any given concentration of acid can be foretold and controlled. It has further proved that with slight variation of constants the same laws hold good for all animal tissues, and the work done will not merely be useful to tanners, but will throw important light on many physiological problems, such, for instance, as the causes of muscular contraction.

The work now in hand is related principally to the electrical relations of swollen and unswollen hide, and seems likely to throw some light on the function of the small quantities of acid present in tan-liquors on the fixation of tannin.

In addition to the Professor's work, a young American chemist,

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Mr. J. A. Wilson, of Milwaukee, the first research student, is working on the swelling of hide with lime and alkalies, and Messrs. Stiles and Jorgensen of the University's Botanical Department, are experimenting on the swelling of vegetable jellies with acids as compared with the behavior of gelatine. It is also probable that Mr. F. C. Thompson, B. Sc., will make use of the laboratory during the Christmas vacation for the study of some of the derivatives of vegetable tannins. This record in so short a time is encouraging, and it is to be hoped it may be continued and expanded in the future.

The honorary degree of Doctor of Science, D. Sc., was conferred on Professor Procter on November 17th at a congregation of the University of Leeds. (The Chancellor's address on that occasion was published in the January JOURNAL.)

TANNERY PROBLEMS FOR TANNERS AND CHEMISTS, II.

By W. R. Cox.

To you who read the February number of the JOURNAL, it may seem that the beam house was disposed of very easily. I do not want to give this impression; I want to try to group the different beam house methods for different classes of leather and to pick out the points for discussion in each of them. In this, I am glad to state I shall be given ample data by the tanners, who are, I believe, interested in these discussions. We will now take up dry hide soaking and liming.

There are several kinds of dry hides, but I believe the ones which are the greatest problem to soak easily and successfully are the sun-dried, or rather sun-baked hides from South America, China or India. For sole leather these hides are usually soaked in cold water (in some cases, sulphide of sodium, borax, soda or formic acid is used in varying quantities) until pliable and then placed in fulling stocks and milled until soft. I wonder how many tanners have ever taken the trouble to find out how much gelatin is lost in the fulling stocks. This is hide substance and if left in the hide and tanned would make more leather in the finishing room.

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Where dry hide sweat sole leather is made, the hides are soaked and then placed in sweat pits until the hair slips, when the hide is unhaired and in some instances given a light liming, and in some worked to the yard without liming. Some sole leather tanners still use the sweat pit and will tell you of its many advantages and good points. If these tanners are right, why do any tanners lime the hide? And then another question comes up, why do we use lime at all?

What does lime do?

What is its function?

How does it remove the hair?

What action does it have on the fat in the hide?

Does it form a lime soap with the fats? If it does, is this a good thing for the subsequent processes, or the leather produced?

All of these questions may seem entirely out of place, but I wish to get the tanner to the point where he will ask himself why he is doing certain things in a certain way, year after year, never stopping to think whether there is any other way; and why, if some new ideas are advanced, they are condemned as of no use because they are radically different from what they are accustomed to.

Of course we must remember that a tanner is working with a raw material which is expensive, and which, if spoiled, is a dead loss. The chemist must remember that in the iron and steel industry the results of mistakes can be remelted and nothing lost but labor, and the same is true in various industries, but mistakes in tanning always mean a monetary loss. But has anything in science ever been achieved without loss, and are there not countless instances where mistakes have meant the opening up of vast ideas and developed into wonderful results?

Now to get back to soaking dry hides. Will not the chemist experiment along the lines of assisting the tanner to soak a dry hide in water, or in a mild solution of one of the alkalies or the acid previously stated, until it is pliable? Then will he not show the tanner how to take this hide, and in some solution which will work in conjunction with the process of liming, etc., to follow, drum it and have it take up water to saturation in 30 minutes?

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This can be done, and if the chemists wish, data can be furnished them for a basis to work out a scientific method from one which is now practical to a certain extent, but could be improved by the chemists if acting jointly.

Now to the tanner and beam house foreman, use your brains. You have to-day for unhairing, lime, sulphide of sodium, arsenic, caustic soda and sulphur. If you are using lime, how much per cent. are you using? If 6 per cent., why? If you believe in excess of lime in the pits, why do you? How often do you clean your limes? How do you make your fresh limes? What is the difference in the finished leather if all fresh limes are used, or all old ones, and why is the leather different? There is a reason. We need the help of the chemists for research, but first let the tanner search himself and look around. Think and act. Do not slide along in the same old way, but know what is going on, and why, and when you do, the chemists will be of assistance to you and you to them. If it can be proved that lime is not necessary in the making of leather we can make, easily and quickly, a big step in the beam house, by unhairing with paste from the flesh, and in this way every hide will be uniform, and we would save all the hair (which is quite an item) clean and strong. Some tanners will state emphatically you cannot make good leather without lime. Are you sure? Are you qualified to state as a finality that it cannot be done?

Next month various beam house combinations will be presented and discussed with different opinions for different leathers. Remember this JOURNAL is open to print discussions along any tanning ideas, and the A. L. C. A. will, I believe, welcome tanners' ideas and reply to them.

NOTE:—See the article in volume 7, 1912, A. L. C. A. JOURNAL, p. 467, Use of Formic Acid in Soaking Dry Hides, by J. R. Blockey, M. Sc.

COLLEGIUM.

The first number of the new London edition of *Collegium*, dated Jan. 12th, has been received. The editors are Mr. M. C. Lamb, F. C. S., and Prof. E. Nihoul, both well and favorably known through their work on this side of the Atlantic. The

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following gentlemen are named as honorary abstractors: W. R. Atkin, H. Brumwell, S. Hirst, E. F. Holyoak, R. F. Innes, W. James, E. Merry, W. A. Sowray, and D. Woodroffe. The office of publication is 176 Tower Bridge Road, London, S. E. The number contains four original papers. Those by Professors Procter and Nihoul ("The Combination of Acids and Hide-substance" and "Estimation of Nitrogen in Hide") are both to be continued. That by Alfred Seymour-Jones appears in abstract in this number of the JOURNAL, and that by H. G. Bennett will be published in the April JOURNAL, ("Note on the Analysis of Cube Gambier"). A number of good abstracts are included, most of them being in both English and French.

ABSTRACTS.

A Contribution to the Question of the Distinction and Detection of Tanning Materials and Cellulose Extract in Leather. R. LAUFFMAN, Assistant in the Freiberg Institute. *Ledertechnische Rundschau,* Dec. 24 and 31, 1914. It is often a matter of importance to be able to determine what kind of tanning material was used in the manufacture of a given piece of leather. Tannin undergoes certain changes in the process of leather formation, by oxidation, decomposition, etc. It is a question therefore whether the tannin present in leather can be recognized by the same tests which would be available for the extract which was used in making the leather, or whether the chemical character of the tannin originally present in the raw material or extract has so changed as to make these tests inapplicable or unreliable. A series of experiments designed to throw some light on this matter has been undertaken at the Freiberg Institute at the suggestion of. Dr. Paessler. A number of samples of leather were made with extracts of quebracho, mangrove, chestnut and cellulose. The last-named was the "Hansa" brand. These were chosen because they are easily distinguishable by characteristic tests. Nine leathers were made: No. 1 with quebracho, No. 2 with chestnut, No. 3 with a mixture of quebracho and chestnut, No. 4 begun with quebracho and finished with chestnut, No. 5 begun with chestnut and finished with quebracho, No. 6 with a mixture of quebracho and mangrove, No. 7 with a mixture of quebracho and cellulose, No. 8 begun with quebracho and finished with cellulose, No. 9 begun with cellulose and finished with quebracho. In the mixtures the proportion of each material was approximately 50 per cent. The first stage of tannage was carried out in small handlers, and the second stage in a rotating bottle, in the manner of a drum. The strength of the liquors in each case is shown in the table, in Baumé degrees. In each case the liquor started at the

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lowest figure and was strengthened from time to time by addition of solution containing 10 per cent. tannin, reaching the highest figure at the close.

TABLE I.

Leather number	1	2	3	4	5	6	7	8	9
Liquor in handlers	0.15	0.10	0.10	0.10	0.20	0.10	0.10	0.10	0.20
	0.60	0.90	0.80	0.60	0.95	0.70	1.70	0.60	2.65
Liquor in drum	0.85	1.15	1.10	1.90	1.20	1.00	2.30	0.90	3.60
	6.80	8.90	7.80	9.20	6.30	7.60	11.50	20.00	6.40

All the leathers stayed in the handlers 5 days. The drum treatment of numbers 1, 3, 4, 5 and 6 lasted 20 days, and that of the others 23 days. At the end of tannage, the leathers were rinsed in water and dried. A sample of each was ground, and 100 grams extracted in a Koch flask to 2 liters in 3 hours, this solution being used in testing for the various tannins. The results of these tests are shown in Table II. The quebracho and mangrove extracts used proved to be pure, but the chestnut varied in several respects from the standard. A pure chestnut tested by the formaldehyde reaction remains quite clear, while this showed a slight cloudiness. The soluble solids of the extract in question showed a solubility figure in acetic ether of 47, while pure chestnut gives from 3 to 17. The molybdenum figure of pure chestnut is from 182 to 225 instead of 87. These differences would make it appear that the extract in question contains myrobalans. The cellulose extract was quite characteristic.

The author discusses at some length the results of the tests for each leather. Numbers 1 and 2, tanned throughout with quebracho and chestnut respectively, show results so similar to the extracts used that there would seem to have been no marked change in the chemical characteristics of these materials during the tanning process. In the other 7 cases, the leathers having been made with two materials, the tests show approximately in what proportions the two materials are present in the water extract. The extract from 3 more nearly resembles the chestnut extract, from which the author concludes that the quebracho tannin is more firmly held by the hide. A similar conclusion is drawn in regard to No. 4, where the quebracho and chestnut were used separately. In the case of No. 5, however, where the chestnut was used first, the reactions of the water extract more nearly resemble those of quebracho, indicating that the chestnut is more firmly held when used for the first stage of tanning. No. 6 gives tests which are about an average between those of the quebracho and mangrove extracts, indicating that the two materials were fixed in approximately equal parts. This operates against the idea frequently expressed that mangrove tannin is of little value. The extract from No. 7 showed characteristic tests for a catechol tannin, due to the quebracho, but there was no precipitate with bromine water. It has been shown that the presence of sulphite-cellulose extract prevents the bromine precipitate from forming. The strong Procter-Hirst reaction shows sulphite-cellulose present in the leather extract, and the fact that the

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TABLE II.

			Leather number					
			1	2	3	4	5	6
Formaldehyde reaction.	Heating with formaldehyde and HCl.		complete precipitation	slight cloudiness	slight precipitation	slight precipitation	precipitation	complete precipitation
	Iron alum and sodium acetate added to filtrate, or to unprecipitated solution.		not blue	blue	blue	blue	blue	not blue
Lead acetate reaction in acetic acid solution	On addition of lead acetate.		no precipitation	precipitation	precipitation	precipitation	slight precipitation	no precipitation
	Color of filtrate or clear solution on adding	Iron alum.	gray-green	blue	blue-green	blue	gray-green	gray-green
		Iron alum and sodium acetate.	blue	blue	blue	blue	blue	blue
Bromine water reaction			precipitation	no precipitation	slight precipitation	slight precipitation	precipitation	precipitation
Acetic ether solubility number	Of soluble solids		62	42	53	51	60	50
	Of tanning matters		72	49	60	59	70	58
Tannin acidity number			24	215	155	120	78	24
Sulphuric acid reaction			carmine red	light brown	carmine red	carmine red	carmine red	carmine red
	after dilution		bright red	nearly colorless	bright red	bright red	bright red	bright red
Procter-Hirst reaction for cellulose			none	none	none	none	none	none
Molybdenum number								
100 cc. of the water extract contained (*g*)	Tannin		0.22	0.34	0.20	0.26	0.20	0.22
	Non-tans		0.06	0.15	0.05	0.09	0.05	0.07

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TABLE II.—(*Continued.*)

			Leather number			Extracts used in making leathers 1 to 9			
			7	8	9	Quebracho	Mangrove	Chestnut	Cellulose
Formaldehyde reaction	Heating with formaldehyde and HCl		precipitation	precipitation	precipitation	complete precipitation	complete precipitation	slight cloudiness	no precipitation
	Iron alum and sodium acetate added to filtrate, or to unprecipitated solution		not blue	not blue	not blue	not blue	not blue	blue	no distinct coloration
Lead acetate reaction in acetic acid solution	On addition of lead acetate		no precipitation	no precipitation	no precipitation	no precipitation	no precipitation	precipitation	no precipitation
	Color of filtrate or clear solution on adding	Iron alum	gray-green	no distinct coloration	gray-green	gray-green	gray-green	blue	no distinct coloration
		Iron alum and sodium acetate	blue	blue	blue	blue	blue	blue	no distinct coloration
Bromine water reaction			no precipitation	no precipitation	precipitation	precipitation	precipitation	no precipitation	no precipitation
Acetic ether solubility number	Of soluble solids		42	22	59	67	18	47	15
	Of tanning matters		50	29	67	76	19	55	16
Tannin acidity number			55	70	36	19	16	215	75
Sulphuric acid reaction			carmine red	red	carmine red	carmine red	red-brown	brown	brown
	after dilution		bright red	pale red	bright red	bright red	brownish-yellow	pale brown	colorless
Procter-Hirst reaction for cellulose			reaction	reaction	slight reaction*	none	none	none	slight reaction
Molybdenum number						11	105	87	0
100 cc. of the water extract contained (*g*)		Tannin	0.22	0.22	0.25				
		Non-tans	0.14	0.45	0.07				

* Distinct reaction after 15 minutes.

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tannin acidity number is between those of quebracho and sulphite-cellulose, as is also the acetic ether solubility number, indicates that the two materials are present in nearly equal amounts in the extract from the leather, and therefore both have been taken up by the hide. In the extract from leather No. 8 the tests are similar to those of 7, except that the ether solubility number and the tannin acidity are much closer to those of cellulose extract than to those of quebracho. This seems to show that the sulphite-cellulose, which was used in the second part of the tannage, was less firmly held by the hide than was the quebracho tannin. In the case of No. 9 the tests were in most respects like those of quebracho extract. The solubility figures and the tannin acidity were near those of quebracho, and the Procter-Hirst test gave a distinct reaction only after some time. This seems to show that when sulphite-cellulose is used in the early stages of tanning it is firmly fixed by the hide. To sum up, when a leather has been made by beginning the tannage with one material and finishing it with another, the leather extract resembles the latter more than the former. If the practical value of a tanning material depended only on its ability to be taken up and fixed by hide, sulphite-cellulose would seem to contain real tannin. The excellence of a leather depends, however, on other properties in the tanning material as well as its power to be fixed by hide, and in one or another of these other properties the various kinds of sulphite-cellulose extracts are deficient.

When the materials used in the tannage of a given leather are unknown, the water extract of the leather cannot be depended on to give complete information in regard to the materials used, because a part of the tannin may be so firmly bound to the hide fiber that it does not appear in the water solubles. By using alkaline solution to leach the leather, it is possible to remove from it other portions of the tanning material, and then by neutralizing the solution with acetic or other weak acid it may be brought into condition to be tested. It is far from certain that the tannins will not suffer alteration by such treatment, so that the application of such a method will be in general of doubtful usefulness. The mixtures used in modern practice present many and serious difficulties. Modification of some of the tests may result in throwing further light on the general problem. The solubility of a material in acetic ether is of less value than the solubility of the tannin of the material, because the proportion of tan to non-tan will in general not be the same in the case of the original material and of the matter dissolved out of the leather. The acetic ether solubility of the tannins, as given in Table II is found by subtracting the solubility of the non-tans from that of the total solubles. The molybdenum number of the leather extracts is not given. The solution for this purpose must be of 4 times analytical strength. Such a solution can only be made from the leather extract by evaporation. The results obtained from evaporated solutions were so abnormal that the author concludes that the tannins had undergone important changes in the process of evaporation. He proposes to investigate the molybdenum numbers of various materials in more dilute solu-

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tions. The author now reviews the tests shown in Table II and shows what conclusions could be drawn from them if nothing were known about the materials which had been used in making the leather. He then goes on to discuss the detection of sulphite-cellulose in the leather extract of leathers which have been tanned with mixtures containing sulphite-cellulose. Dr. Gansser (*Collegium*, 1912, p. 482; abstr. this J., 1912, p. 635) found that when sulphite-cellulose to the amount of 5 per cent. or even 2 per cent. of the total tanning matters was used in the manufacture of leather, it could be detected in the water extract from the leather. F. M. Loveland (this JOURNAL, 1913, p. 133) finds no reaction by the Procter-Hirst test in the case of leathers tanned with sulphite-cellulose. Dr. W. Moeller (*Collegium*, 1914, pp. 152, 319, 382, 488; abstr. this J., 1914, p. 246) finds that when the sulphite-cellulose is used in the early stage of tannage it becomes firmly fixed on the fiber and does not wash out. If, however, it is used as a filler, the leather extract shows the reaction of the Procter-Hirst test. Dr. Moeller has later worked out a method, by which he treats the leather with a 2 per cent. solution of caustic soda for from 12 to 24 hours in the cold, then adds HCl to feeble acid reaction, filters off the precipitate and applies the Procter-Hirst reaction to the filtrate. The three leathers of the series described at the beginning of this article which contained sulphite-cellulose were tested by both the Procter-Hirst method and by that of Appelius, both immediately after tannage and at the end of 3 months. The results are given in Table III.

TABLE III.

		Immediately after tannage			3 months after tannage		
		Leather number			Leather number		
		7	8	9	7	8	9
In water solution extracted from the leather	Procter-Hirst	reaction	reaction	slight reaction*	reaction	very slight reaction*	very slight reaction*
	Appelius	reaction	reaction	slight reaction	reaction	slight reaction	slight reaction
In the alkaline solution, neutralized and filtered (Moeller)	Procter-Hirst	reaction	reaction	no reaction	no reaction	no reaction	no reaction
	Appelius	reaction	reaction	slight reaction	no reaction	no reaction	no reaction

* Distinct after 15 minutes.

The Appelius method is that of Appelius and Schmid (*Collegium*, 1914, p. 597; abstr. this J., 1914, p. 566). The paper closes with a discussion of the reactions of neradol D and neradol N with a table of results. L. B.

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Experiments with Sudanese and Libian Skins. Compiled by Consul W. RODERICK DORSEY from a report of the Director of the Experiment Station for the Skin Industry at Naples. *Consular Reports.* The annual production of oxen in Tripolitania is about 50,000. They are small, weighing, on an average, 661 pounds. The Royal Experiment Station for the Skin Industry, at Naples, received from Tripoli 10 specimen cowhides, dry salted, which averaged 20.9 pounds, only 2 weighing less than 13 pounds, and 4 calfskins that totaled 24.3 pounds. Cirenaica sent 17 cowhides and 11 calfskins, whose weights averaged 15.4 pounds and 6.6 pounds, respectively. Those from Cirenaica were of better quality and more evenly assorted. The fiber and substance were uniformly good, with softness and strength about equal. Some defects were observed, however, which it seems should not be difficult to overcome. The principal blemishes were scratches caused by careless and hurried skinning, but in some the quality on the upper surface was poor, owing to bad curing, and sometimes they showed scars and marks of branding with fire. To a smaller extent some were pierced by cattle flies (*Hyperdoma bovis*), causing defects which, by their nature, will be much more difficult to prevent. But, as the skins under experiment are of comparatively light quality, a grade that is scarce on the market, we think they merit the careful attention of consumers, more especially as many of these defects are susceptible of being eliminated at no distant date. Taking into consideration the quality and weight of the skins, only part were sent to be tanned by the chrome process which, more than any other, makes faults visible. Others, too light to give a useful surface if split and too heavy for chroming, were treated by the English tank system for 4 weeks, with oak bark and extract of chestnut and quebracho, and afterwards, for a further 2 weeks, in a ditch with pure African cork. The heaviest and least perfect skins were prepared for soles, and others for finishing with wax by the usual processes. The rearing of goats is much practiced in Tripolitania, where the animals are of medium size with black or reddish hair, have small, sparsely covered tails, and measure at the withers 24 to 26 inches. Under the wool a soft down grows that is used by the natives in weaving materials for local use. A full-grown goat weighs 66 to 88 pounds, and kids, which are sold very young, 11 to 15.4 pounds. During the 4 months, July to October, 1913, untanned goatskins weighing 63,550 pounds were exported from Tripoli and vicinity. The Royal Experiment Station has also received, at various times, nearly 10 dozen of these skins from both Cirenaica and Tripolitania, which, after freshening and cleansing, were sorted. One lot was dressed *"a chevreaux,"* black; others that did not lend themselves to such fine treatment were submitted to various experiments that gave interesting results. Some were tanned by the English "semi-chrome" system, and after the usual operations of the beam house and being placed in a dung bate, were treated on reels with gambier and then placed in casks containing a basic chrome liquor. The operation, therefore, was the same that is used for the vegetable tanning of upper leathers and these skins acquired a great

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compactness and substance as well as good body and a high gloss. Others were subjected to the special "Dongola" process, a term used in America to indicate tanning with alum and gambier combined, but this experiment has not yet terminated. Still others were prepared, as cheap morocco, that is to say, tanned in casks with sumac, gambier, and quebracho, and afterward colored—black, Bordeaux red, blue, and dark green—with aniline dyes, tartar emetic, and "coricromo" being used as mordants. Finally, a few to be used as linings, etc., were tanned with alum. The experiments with the goatskins have shown that they are of good quality and substance without too much refuse and with few diseased pelts. In the exportation of sheep from Tripolitania, which reaches nearly 100,000 head a year, three kinds are noted—those from Orfella, with slender tails; those from the Gebel, with fat tails and short legs; and those from the Sudan, of great size but little wool. At Tripoli there are many sheep of medium stature with gross tails, whose fat is greatly liked by the natives. Fleeces would be ample and uniform if the animals were well cared for, but, considering that the natives are very negligent about their raising, skin maladies abound, causing a partial falling of the wool. The average weight of the Tripolitan sheep is nearly 77 pounds, that of the rams 88 pounds, while lambs from 4 to 6 months old run to 39.6 pounds, those over 1 year reaching 61.7 to 66 pounds. In the 4 months July to October, 1913, sheep and lamb skins weighing 115,156 pounds were exported from Tripoli and vicinity. The skins placed at the disposal of the experiment station, numbering about 50, were of varying qualities and sizes, which caused no little difficulty, it being necessary to make many small subdivisions for the processes that best suited the several skins. Specimens from both Cirenaica and Tripolitania were included. Two skins were cured for rugs in the usual way with the hair on. Of the others, intended for gloves, those of best quality were treated with lime and arsenic and the wool was removed. The rest were placed directly in lime and, after the customary time, deposited on trestles to remove the wool. Afterwards the pelts were again assorted, those adapted to the making of gloves to be tanned with alum, flour, yolk of egg, and salt, the others to be treated in casks with extracts and then dyed and dressed with tannin as sheepskins with a glossy black surface. After the glove skins were finished they were again sorted, those of greater body and substance suitable for tan and long white gloves for women being divided from those of lower quality—rough, oily, and scabby—which may be used advantageously in the production of skins pumiced on the flesh side in imitation of genuine suedes. This is also a branch of the industry that merits a long, accurate, and careful examination. The following grades of wool were derived from the above-named skins: Arsenicated—dirty white, washed white, and washed gray; limed—white superior, white inferior, and gray. Camel skins from Libia do not form a very important article of commerce, because the animal serves as a means of transport and therefore only the skins of such as die or are slaughtered for food are brought to the market. From July to October, 1913, exports from

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Tripoli and vicinity amounted to 11,389 pounds. But little known, these skins, present a type irregular in the extreme. They are full of cuts, holes, scratches, callouses, scabs, scars, and marks of fire, and are removed from the carcass in an entirely special manner, that is to say, by cutting from the rump instead of from the belly. Those of Cirenaica are in little better shape, without head and feet. To gain an idea of the irregularity and peculiar structure of these skins two were tanned entire, one from Cirenaica, by the English tank and ditch system already mentioned, and the other, from Tripolitania, by extracts in casks. They were afterwards oiled to try to finish as leather for uppers. These experiments were made purely for purposes of demonstration. As camel skins have a very low value (they scarcely ever reach $6.13 per 100 pounds) the others were halved and tanned by the English tank and ditch system in the same manner as cowhides. The skins so cured, showing all the defects named, can be used for soles, especially at this time when the market is high. A somewhat limited use that can be made of camel skins tanned with chrome is the manufacture of shoe laces and a special kind of girth sometimes seen on the market and known as the "Magaldi" girth.

Photomicrography. ALFRED SEYMOUR-JONES. *Collegium*, London Edition, Jan. 12, 1915. For most purposes the most suitable size of plate is 3¼ by 4¼ inches. The set of objectives used by the author includes 35 mm., 24 mm., 10 mm., 3 mm. and 1/16 inch oil immersion. The first is well adapted for the photographing of leather grains and other opaque objects whose surfaces are not plane, on account of its "depth of focus." For stained sections the 24 or 10 will usually be better than higher powers. The arrangement of apparatus recommended and illustrated by a number of cuts is vertical. It consists of a heavy iron foot-plate with two upright rods to hold the camera, which has an extension of 18 inches. Minute directions for operating are given. The reproduction of a photomicrograph of a goat grain is excellent. The article is to be continued.

Procter Research Laboratory. H. R. PROCTER. in *L. T. R.* (letter to the Editor). I may draw the attention of your readers to the provision made by Leeds University for technical research. Anyone who has a reasonable knowledge of chemistry, and who desires to work out a technical problem for business purposes, may apply to be received as a technical research student at a fee of two guineas per month, and will have the use of all our work-shops and laboratory appliances, and the best confidential expert advice which we can give him. We have already had several such students who have obtained results of considerable commercial value to themselves. A very advanced knowledge of chemistry is not always necessary, as that we can supply, but such a student must have sufficient practical acquaintance with his special branch to know the common methods, to be quite clear as to what he wants and able to judge whether he has obtained it, and to be capable of working for himself. Raw materials must generally be provided by the student.

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LLOYD BALDERSTON . . . . . Associate Editor

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TWELFTH ANNUAL MEETING OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION.

The Twelfth Annual Meeting of the American Leather Chemists Association will be held at Atlantic City, N. J., on Thursday, Friday and Saturday, May 27th, 28th and 29th, 1915. Headquarters will be at the Hotel Marlborough-Blenheim, where a suitable room will be reserved for our meetings. Those planning to be present at that meeting, should apply directly to the hotel management for reservations, AS EARLY AS POSSIBLE. The date of our meeting coming so near a holiday, makes this early reservation imperative, in order to be sure of your room. The rates at this hotel are as follows:

European Plan—

1 room, 1 person, $3.00 and $4.00
1 room and bath, 1 person, $4.00, $5.00 and $6.00.
1 room, 2 persons, $5.00 and $6.00.
1 room and bath, 2 persons, $6.00, $7.00 and $8.00.

American Plan—

1 room, 1 person, $5.00 and $6.00.
1 room and bath, 1 person, $6.00, $7.00 and $8.00.
1 room, 2 persons, $9.00 and $10.00.
1 room and bath, 2 persons, $10.00, $11.00 and $12.00.

H. C. REED, *Secretary.*

BOUND VOLUMES OF THE JOURNAL.

Copies of all the back volumes of the JOURNAL are on hand, bound in one-half morocco or cloth. These will be exchanged for unbound numbers in good condition at the rate of $1.20 per volume delivered, if the unbound numbers are sent by mail or express prepaid to the manager at Ridgway, Pa. Missing numbers will be supplied at 25 cents each. Members who have joined the Association recently and so have not the earlier numbers to exchange, may procure the bound volumes at $4 per volume delivered, on application to the manager.

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CHEMICAL DATA FROM THE PICKLE SOLUTION

By P. M. Randall.

The following are some simple curves obtained from the tannery, a special set or pack of pelt being run and samples taken at intervals, so as to obtain results from which to plot the following curves. Leaking doors and trunnions prevent an absolute quantitative determination, but the following curves are the results of several tests carried out under tannery conditions.

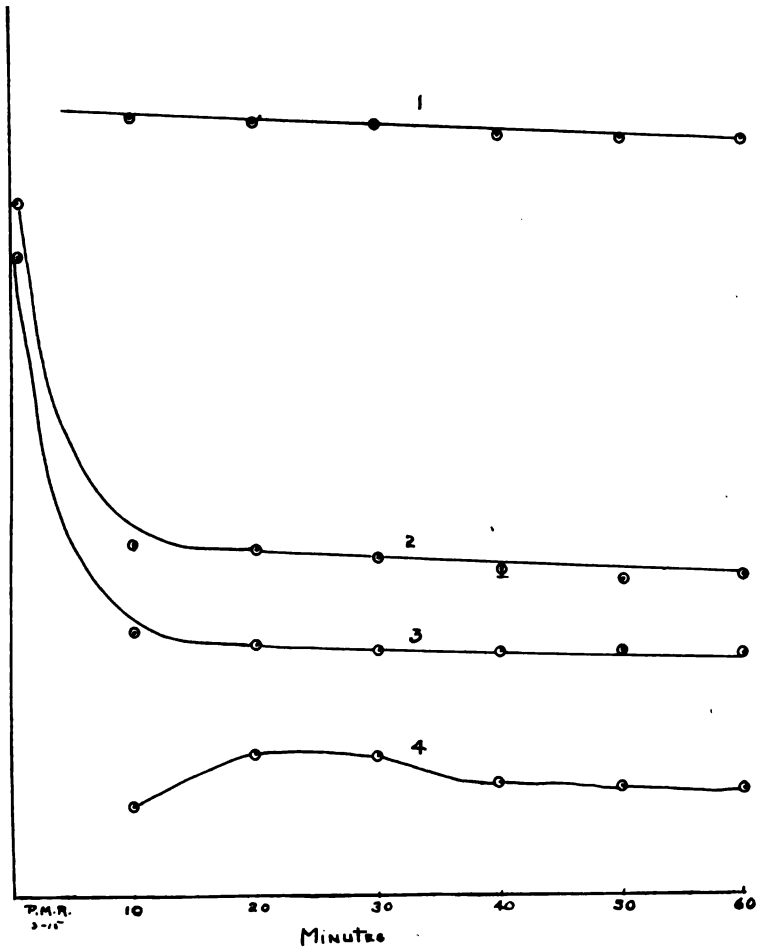

CHART I

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The object of these curves is to show the action or occurrence in proportion of salts during the process of pickling.

Curve 1, Chart 1, shows the loss of moisture in pelt during the pickling process, due principally to the dehydrating power of the precipitated colloids or mineral salts.

Curve 2, Chart 1, indicates the rapid absorption of the SO ions present by the pelt, during the pickling process and the greatest amount of absorption happening within the first 10 minutes of operation. The same can be said of Curve 3, Chart 1, which rep-

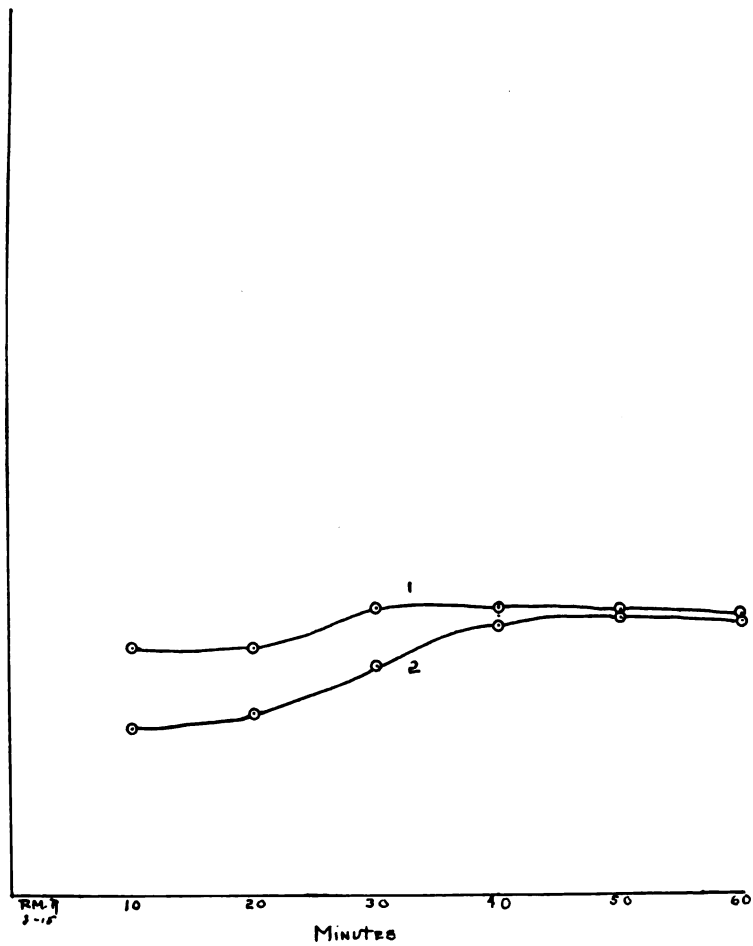

CHART 2

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resents the total amount of chlorine present. I give this in terms of total chlorine as there is a possibility of ammonium chloride, calcium chloride, hydrochloric acid and sodium chloride being present.

Curve 4, Chart 1, shows the action of hydrogen sulphide liberated by the action of sulphuric acid on the sulphide salts present, mainly ammonium sulphide; these compounds being present in the pelt as the pelt had been previously treated with sodium sul-

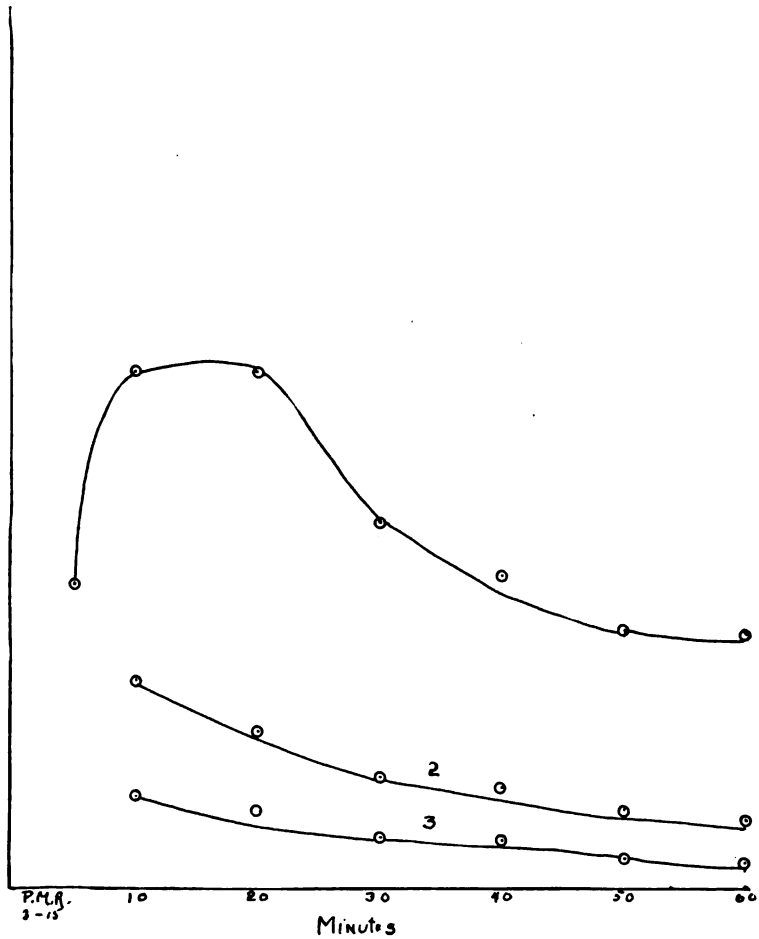

CHART 3

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phide and ammonium salts. The sulphides in solution are greatest after the first 10 minutes of operation and then gradually dropping off due to the escape of the gas from the mill.

Curve 1, Chart 2, shows the total calcium present in solution during the pickling. It has a tendency to show the bating effect of the pickle or the power that the pickle has to remove lime from the pelt.

Curve 2, Chart 2, shows the rate of formation of calcium sulphate which is kept in solution by the excess of sodium chloride present and that practically all the calcium is present as calcium sulphate at the end of the operation. These curves were made from a filtered solution. There being quantities of hide fragments present in the solution I could not get good results from an unfiltered solution.

Curve 1, Chart 3, represents the hydrogen sulphide gas in the mill; that is that which is not absorbed by the solution. The same with Curves 2 and 3.

The three different curves represent three weights of leather or pelt. The first being very heavy leather, the second medium, and the third light. The greatest quantity of gas is seen to be during the first 10 minutes of operation after which the gas gradually escapes through the doors and trunnions.

All these curves are taken from side leather stock pickled with sulphuric acid and salt in a mill for one running hour and the samples taken at every 10-minute interval.

Laboratory of the Widen-Lord Tanning Co.

REPORT OF MOELLON COMMITTEE.

By T. A. Faust, Chairman.

The results of the collaborative work carried out by the committee last year indicated the necessity of revising some of the methods, so that more uniform results would be obtained by various operators. The procedure for moisture, ash and free fatty acids was satisfactory, and excepting a re-writing of the methods according to the suggestions of the members of the com-

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mittee, no laboratory work was done on these determinations this year.

The methods for unsaponifiable and oxidized fatty acids gave unreliable results last year, and the chairman accordingly rewrote these methods, taking into consideration the various objections offered, and submitted them to the collaborators. A sample of moellon containing 10 per cent. wool grease and 10 per cent. mineral oil was sent to each member, and the determination of unsaponifiable and oxidized fatty acids by the revised methods requested. The results of the various operators are published in the accompanying table.

Unsaponifiable.—It will be noted that the results on unsaponifiable agree very well, and it is therefore apparent that this method is dependable.

Reed and Norris stated a preference for the use of sulphuric ether, but the work carried out by the committee last year indicated petroleum ether to give more concordant results on the same sample by different chemists.

Orthmann objected to the method for samples containing wool grease, claiming more accurate results by the use of sodium ethylate.

Sprague and Veitch mentioned the losses liable to occur by excessive drying, and a clause was added to the method embodying their suggestion.

Small and Alsop suggested writing the methods in the imperative mood.

Eachus reported the method entirely satisfactory.

Esten suggested the use of a larger quantity of alcohol, thereby lessening the troubles from emulsions; and also suggested a more definite wording.

Oxidized Fatty Acids.—The results for this determination (see table) showed a poor agreement, there being a difference of over 4 per cent. between the high and low results; there is however, an improvement over the results of last year's committee.

A résumé of the various suggestions for improving the method is herewith given.

Sprague gave the results of some experiments regarding

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length of time for evaporating and drying, and found that placing the dish in an ordinary combined evaporator and dryer for 16 hours gave the most concordant results. He found it necessary to filter the petroleum ether solution of the oxidized fatty acids.

Small suggested roughly defining the volume of the soap solution.

Eachus stated the necessity of properly washing the oxidized fatty acids, and suggested the use of boiling water, so that absolutely all the salt and oil is removed.

Esten preferred allowing the acidified solution to stand over night, claiming a better separation.

Alsop found an additional separation of oxidized fatty acids in the acid wash water that stood over night. Filtering the alcoholic solution of the acids showed a slight loss.

The chairman carried out some work to determine the cause of the discrepancies, and tried out the various suggestions offered by the collaborators. The following facts were noted:

I. No difference was observed when the HCl was added to the soap solution in the beaker and boiled, then transferred to the separatory funnel, or when the soap solution was transferred to the separatory funnel before the acid was added. Boiling the acidified solution probably liberates more completely the fatty acids, but evidently increases their solubility in the acid water.

II. Using a large excess of HCl gave slightly low results; even a 25 per cent. excess causes a distinct loss, by solution of the fatty acids in the wash water. This loss can be neglected, although in some instances it was found to be as high as 0.6 per cent. However, it is doubtful whether these acids, which appear on boiling the acid waters, or on standing some time, exist in the moellon as oxidized fatty acids.

III. The entire operation should be carried through without delay.

IV. The use of hot water in washing insures removal of salt, although care must be exercised when adding the ether. It is very likely that the poor results are due to a large extent to improper washing.

V. If the oxidized fatty acids do not congeal so that the ether and wash waters can be removed without loss of oxidized fatty

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acids, filtration is necessary, the insoluble matter being washed on the filter, dissolved in alcohol, and added to the main portion. On the other hand, when the oxidized fatty acids congeal in a single large lump, special care must be used in washing the oil and salt from the mass.

VI. Evaporating and drying over night does not cause any oxidation, and is preferred as being more convenient.

The method was therefore re-written in accordance with these facts, and together with the remainder of the methods, is herewith submitted to the Association.

PROPOSED METHOD FOR ANALYSIS OF MOELLONS.

Moisture.—Weigh accurately 3 grams of the sample in a wide platinum dish, and heat with a low flame until the moisture is all driven off. This point can be determined by the appearance of smoke, and a slight crackling sound. Place the dish in a desiccator, cool and weigh.

Ash.—Ash the moellon remaining in the dish after the moisture determination in the usual manner, cool and weigh.

Unsaponifiable.—Weigh accurately in a 300 cc. flask, 5 grams of the moellon, add 2.5 grams caustic potash dissolved in a little water (or 5 cc. of a 50 per cent. KOH solution), and 25 cc. of 95 per cent. alcohol, boil with reflux condenser for one hour, shaking occasionally. Glass beads may be used to prevent bumping. Add 50 cc. hot water, cool, transfer to a separatory funnel, and extract three times, using 40 cc. petroleum ether for each extraction. A little alcohol may be added to break persistent emulsions. Wash the combined ether solutions three times with a mixture of 30 cc. of water and 10 cc. of alcohol, transfer to a tared dish, evaporate to dryness, cool and weigh. Excessive drying must be avoided.

Oxidized Fatty Acids.—Boil the soap solution remaining from the unsaponifiable determination until all the alcohol is expelled, then dissolve in hot water, transfer to a separatory funnel, rinse the beaker thoroughly into the funnel, bringing volume to approximately 300 cc., and immediately add a slight excess of concentrated HCl (about 25 per cent. more than sufficient to neutralize total alkali). Rotate the contents of the flask vigor-

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ously, cool and shake out with petroleum ether. Run off the aqueous layer, and pour off the ether layer, avoiding any loss of oxidized fatty acids. Wash these acids twice with small quantities of petroleum ether and hot water; dissolve in warm 95 per cent. alcohol, filter if necessary, transfer to a tared dish, and place in an ordinary evaporator and dryer for 16 hours; then cool and weigh. The entire operation should be conducted without delay.

Free Fatty Acids.—Weigh out 1 gram moellon, dissolve in mixture of 20 cc. alcohol and 20 cc. sulphuric ether, which has been neutralized to phenol-phthalein, and titrate with N/10 NaOH, using phenol-phthalein as indicator. Test for mineral acids or alkalies (by adding methyl orange to the water emulsion of the moellon), and if present, make the necessary correction.

1915 MOELLON COMMITTEE.

	Per cent. unsaponifiable		Per cent. oxidized fatty acids		
Alsop & Cuthbert	13.5		9.5	9.1[1]	0.6[2]
	13.4		9.4	9.2[1]	0.4[2]
Small & Vaudrueil	15.0		6.1		
Esten	13.4		5.4		
	13.2		5.8		
Sprague	14.0		8.5		
Eachus	14.3		6.1		
	14.0		6.5		
Orthmann	13.0		6.6		
			7.2		
Faust & Kernahan	13.2		6.6	6.3[3]	
			6.3	6.2[4]	
Veitch & Frey	13.9		6.9		
	13.7		7.2		
Reed & Norris	13.4	15.7[5]	8.2		
		15.8[5]	8.0		
General average	13.7		7.1		

[1] Dissolving oxidized fats in alcohol, filtering, drying and re-weighing.
[2] Recovered from acid water.
[3] Using double quantity acid.
[4] Using Eachus method; *i. e.* boiling after addition of acid.
[5] Using sulphuric ether.

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UNSAPONIFIABLE MATTER IN GREASES.*

By E. Twitchell.

The following method of determining unsaponifiable matter in greases has been in use under my direction in the laboratory of the Emery Candle Co. for five or six years.

Five grams of the sample (or preferably of the fatty acid prepared for "titer test," as this is cleaner) are saponified with alcoholic potash in a dish and evaporated nearly to dryness. A little alcohol is added and then water, and the solution obtained is washed into a separatory funnel. The ratio of alcohol to water in this soap solution should be about 1 : 4, and the total volume of the soap solution 150 to 200 cc. The soap solution is shaken twice with ether, using about 50 cc. each time. The ether extracts are united, washed once with water, then shaken with dilute hydrochloric acid, washed again with water, transferred to a weighed dish, evaporated, dried at 110° C. and weighed. This residue consists chiefly of unsaponifiable matter, but contains fatty acids as the ether has dissolved some soap which is afterwards decomposed by the hydrochloric acid. It is therefore taken up with neutral alcohol and titrated with standard alkali solution. The fatty acids thus found, calculated as oleic acid, are deducted from the weight before obtained.

A third treatment with ether will extract so little more that for ordinary analytical work it may be omitted.

If the fatty acids obtained from the grease, instead of the grease itself, have been used, the result must of course be calculated on the original grease.

This method differs from that of Allen and Thomson, given by Lewkowitsch[1] as his preferred method, only in some details: chiefly the simple and accurate way of correcting for soap dissolved in the ether. Having this correction, it is not necessary to be sparing in the use of alcohol for fear of causing the ether to dissolve soap, but enough may be used to cause an almost instantaneous separation in the funnel of perfectly clear and

* *J. Ind. and Eng. Chem.*, Mar., 1915, pp. 217-8.

[1] Lewkowitsch, Chem. Technology and Anal. of Oils, Fats and Waxes, 5th Ed., Vol. I, p. 458.

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sharply marked ethereal and aqueous layers. A determination of unsaponifiable matter can be easily completed in 1½ hours. Ether has been found to be the best general solvent for a variety of unsaponifiable matters found in fats and the objection that it dissolves some soap disappears when using this method.

The uncertainty as to the molecular weights of the fatty acids found by titration in the residue would lead to error, but when the small percentage of these fatty acids calculated on the original sample of grease is considered it will be seen that this error is entirely negligible, and the fatty acids may be calculated as oleic acid, or, an average molecular weight, as that of tallow fatty acids, may be taken.

The above method of determining unsaponifiable matter, when compared with other methods, has never given lower results. In some cases the results are higher, especially than those obtained where petroleum ether is used as the solvent. That the results are not too high has been repeatedly proven by a careful examination of the extract, particularly for neutral fat and for ethyl esters which might possibly have been formed from a little alcohol remaining in the ether when it is shaken with hydrochloric acid.

The details of this method were worked out by Mr. C. Foerster, who has used it in this laboratory, not only in the daily analysis of greases, but also with good results in extracting fats containing other than the usual kinds of unsaponifiable matter.

Wyoming, Ohio.

LIMITS OF ACCURACY IN ANALYSIS.

By L. Balderston.

There has been a good deal of discussion about limiting the figures given in reporting extract analyses to one decimal place. Perhaps we do not always consider that the important thing in deciding how far to carry a result is not the place of the decimal point, but the number of "significant figures." Suppose a liquor is being analyzed, the soluble solid residue from 100 cc. of dilution weighing 0.601 gram, and the corrected non-tan 0.248 gram.

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The tannin weight in 100 cc. is 0.353 gram. If the dilution for analysis was 125 grams to the liter, the percentage of tannin in the liquor is 2.82 per cent. This result has three significant figures, and if our weighings are certainly correct in the third figure, there is no apparent reason why we should discard the hundredths place. If, however, experience shows that five analyses of such a liquor are likely to give results varying from 2.5 per cent. to 3.1 per cent. tannin, we would be justified in omitting the last figure, and writing 2.8 per cent.

Extracts differ from liquors in that they must be diluted much more, and so a larger factor must be used in the calculation. Suppose a solid extract is dissolved, 6 grams to a liter, giving a soluble solid residue of 0.4322 and a corrected non-tan of 0.0558. The tannin in 100 cc. is then 0.3764, or 3.764 grams per liter. Dividing by the number of grams of extract taken gives 0.6273, or 62.73 per cent. The last figure is obtained by adding a cipher to the weighing as actually made, and if we accept it as trustworthy, we assert, practically, that the weighing is dependable to 0.06 milligram, which is manifestly impossible. In fact, to state the percentage as 62.7 per cent. is to assume that the weighing is dependable to 0.6 milligram, which is quite as close as ordinary practice warrants. When we consider that even a careful analyst is likely to have variations of six or more units in the third place, in working with such an extract, does it not seem even absurd to carry our results to four places?

As an illustration of the fact that figures far to the right of the decimal point may be trustworthy, take the case of the analysis of the solids in water. Suppose a liter of water gives a residue of 0.314 gram. Analysis of this residue shows it to contain 0.2634 gram of lime, the third figure being quite dependable. Not only do we say that 83,9 per cent. of the solid matter is lime, but that the water contains 0.0263 per cent. of lime, except that this is more likely to be stated as 26.3 parts per hundred thousand. It is not absurd to speak of ten thousandths of a per cent. in such a case, because these ten thousandths are based on actual dependable weighing.

The worst cases of absurdity are perhaps those which come from basing calculations on titration, where the whole quantity

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measured is but small, and the substance under analysis has suffered high dilution. We weigh out 10 grams of a chrome liquor, having about 11 per cent. of Cr_2O_3, and dilute to 500 cc. Ten cc. of this dilution are titrated, containing 0.2 gram of the original liquor, requiring 8.8 cc. of N/10 thiosulphate. Multiplying by the chrome value of 1 cc. of thiosulphate, we have 0.0222806 gram Cr_2O_3, and dividing by 0.2, the percentage is 11.1403. Here are ten thousandths of a per cent. again, but what justification have we for them? Our titration measures to 0.1 cc. and it is impossible to be sure that the reading should not have been 8.75 or 8.85. The uncertainty thus amounts to more than 1 per cent. of the quantity measured, and the largest number of significant figures we are justified in using is three, 11.1 per cent. If we had been dealing with a 1 per cent. liquor, diluted five times, the case would have been quite different. Suppose the reading to have been 8.1 cc., giving 0.0205173 gram Cr_2O_3. Dividing by 2, the number of grams of liquor in the 10 cc. titrated, we have 0.01025865, and are justified as before in using three significant figures, 0.0103, or 1.03 per cent.

The two factors to be considered in deciding where to stop in figuring out a result are, first, the degree of accuracy of the method, and second the degree of accuracy of the measurements actually made. An analysis in which variations of 1 per cent. of the quantity being measured are likely to occur because of impossibility of accurate sampling or other reasons having nothing to do with measurement, should for this reason alone be reported only to two places if the significant figures begin with 5, 6, 7, 8 or 9, and to three places if they begin with 1, 2, 3, or 4. If our measurement includes three significant figures, the result may be expressed to a degree of refinement expressed by three figures. Here as before, order of magnitude must be considered along with the number of figures. If a measurement involves the figures 104, and calculation gives a result expressed by the figures 8,963, only the first two figures should be kept. If, on the other hand, the measurement is 769 and the calculation gives 25,376, three or four places may be retained, since 769 is about as many times 254 as 2,537 is times 769.

Sometimes it is necessary to use equivalents extending to a

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number of places which at first glance seems unnecessary, because these equivalents may have to be multiplied by large numbers. Thus the figure used above for the value of 1 cc. of N/10 thiosulphate in Cr_2O_3 is 0.002533. When the number is to be used as a divisor, the accuracy with which it is expressed need not be very high if the number is a large one. If a sample of silver is being weighed out to be analyzed, its weight must be known to a tenth of a milligram, but if we are weighing out 50 grams of lactic acid for the determination of sulphuric acid, it is quite sufficient to weigh it to the nearest tenth of a gram.

TANNERY PROBLEMS FOR TANNERS AND CHEMISTS, III.

By W. R. Cox.

Beam house methods are and must be conducted with the finished leather the tanner wishes to produce as the ultimate object always in view. In making this statement I wish to try to impress on the tanner and chemist what an important, if not all-important, part the beam house methods which are used play in the production of various leathers.

I will now try to group the various classes of leather that could be worked in one beam house, and explain why they can be so worked. For instance, acid and non-acid hemlock, oak or union sole leather, belting butts, flexible sole leather and chrome sole leather could all be limed in one beam house using a high percentage of lime and keeping these limes free from ammonia, that is, keeping them fresh and clean. Sulphide of sodium could be used in small quantities, but care would have to be taken to see that the alkalinity did not offset the action of the fresh limes. For the leathers above mentioned, we require maximum plumpness. This is obtained by liming quickly, and quick liming preserves the greatest possible amount of hide substance. This can be accomplished in three days if sufficient lime is used.

The next group will be harness, skirting, collar, bag and strap, Goodyear welting or upper leather to be tanned in bark or extracts or combinations of vegetable tannins. The liming for these classes of leather should be entirely different and distinct

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from the first group and should take from five to seven days, using lime and sulphide of sodium, lime, sulphide of sodium and calcium chloride, lime and arsenic sulphide, or lime, caustic soda and sulphur, or lime only.

Some reason must be advanced for the necessity of different beam house methods and in this I will try to adhere strictly to the practical results and common sense without entering into a technical discussion of the structure of the hide itself.

In making sole leather we try to get two or three results and they are necessary for success if the leather is to be disposed of profitably. The first and perhaps most important is solidity without extreme brittleness. The second is to have with the solidity enough thickness or "iron" so that your leather will cut to advantage in the shoe factory. The third, color; by that I do not mean any particular degree of fairness, but a uniform and attractive appearance free from spots or uneven color.

The first two we must lay the foundation for in the beam house. By that I mean you could use all the extracts or any extract or any combination of them and not make profitable sole leather were you to lime too long in old limes containing a high percentage of ammonia. If this is the reason for certain results which we know we obtain, then we can analyze what we do to the hide in various beam house methods and try to find the exact point or nearly so; by that I mean a fixed formula for different leathers.

I will assume that we will agree that a hide consists of the outer cuticle, which is the grain when finished, and between this and the flesh a network of fibers, and between these fibers, interfibrillar substance. Short, quick liming in fresh limes does not dissolve much of the interfibrillar substance between these fibers. Consequently, when we bring this hide into the tan liquors, we have more substance to convert into leather and a larger body to saturate and fill with concentrated extracts. But by so doing we destroy to a greater or less extent, as the case may be, the function of the fiber, *viz.*, tensile strength. (I want the readers to assume that the deliming or bating of any of these leathers under discussion are properly done, as these points will be brought out in later articles.) For instance, it is possible to make a

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beautiful glove leather and lime 20 days in old, weak limes, but is it possible to make a sole leather possessing the necessary requirements, *viz.*, solidity and thickness, from such a beam house? You would have a better chance of making a piece of glove from the sole leather beam house than you would the sole leather from the glove leather beam house, because you could, in bating and drenching, take away from the hide, but the fact remains indisputable that it cannot be put back.

This brings us to the point I want to bring out, that all our beam house work is along one line, either to dissolve as much inter-fibrillar substance as we think is necessary to get the maximum stretch to the fibers, to preserve as much of it as possible to get the maximum thickness, or iron, or to try and get the combination of the two, *viz.*, measure and thickness. No methods have been devised so far to get one without sacrificing the other. If I have made myself clear, then I would like the tanner to ask himself whether he is safe in his present beam house methods for the leather he may be making.

To the chemists. Will they not give the tanners some data as to the relative value of different strengths of lime solutions of different age, and what is the ratio of their inter-fibrillar substance dissolving activities as they increase in age and ammonia, or lime in combination with sulphide, arsenic or soda ash?

NOTE ON THE ANALYSIS OF CUBE GAMBIER.*

By Hugh Garner Bennett, M.Sc.

Although cube gambier should undoubtedly be classed under the heading of "extracts," it is very unsatisfactory in analysis to treat it as such. If so treated, the analysis is an exceedingly slow and tedious business owing to the impossibility of filtering it through either the candle or filter paper in any reasonable time. Duplicate analyses, moreover, are apt to differ rather widely, and finally, the amount of insoluble matter even in some No. 1 cubes is such, that there is a distinct error in neglecting their volume when "total solids" are being pipetted.

* *Collegium*, London Edition, Jan., 1915, p. 13.

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If, on the other hand, the cubes be treated just as if they were a dry material, such as myrobalans or valonia, these difficulties disappear.

In the first place, the grinding of the sample makes it possible to obtain a much more homogeneous material, and in this case there is no difficulty in obtaining duplicate analyses which agree. Cube gambier itself is by no means homogeneous, less so perhaps than any other tanning material, so that some precaution of this kind seems absolutely essential for good agreement between duplicates, and between different observers.

In the second place, the extraction in the Procter extractor serves as a coarse filter, and makes it possible to obtain infusions which can be filtered through either the candle or filter paper in an appreciably shorter time. The extraction, of course, need not be nearly so prolonged as with unleached materials, for the soluble matter is soon extracted. No soaking overnight is at all necessary and hot water may be employed from the commencement, so that the preparation of the infusion takes very little longer than when the gambier is dissolved up direct. The little extra time it does need is more than saved by the quicker filtration.

It is necessary, of course, to determine moisture directly, but as mentioned above, there is here a gain in accuracy, for the error due to the volume of the insoluble matter amounts to 0.1 per cent. with some No. 1 cubes and with poorer qualities is of course greater, owing to the very large amount of insoluble matter they contain. There is also a further gain in accuracy by the direct determination of moisture. A considerable proportion of the insoluble matter in a complete gambier infusion settles very quickly, and it is impossible to pipette 50 cc. for "total solids" with any satisfaction even when the infusion is shaken well immediately before pipetting. The pipette also is apt to retain appreciable particles of insoluble matter.

No doubt many of these points have been noticed by other workers, but the advantages of treating cube gambier as a dry material are so distinct that it seems desirable that the I. A. L. T. C., or at least the British section, should agree upon

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this as a general rule of analysis. The concordance and accuracy so obtained would be one further step towards a general agreement to sell cube gambier on analysis,—an agreement which, from the tanners' point of view, is long overdue.

THE ESTIMATION OF NITROGEN IN LEATHER.*

By Dr. E. Nihoul.

The author uses the Kjeldahl method and finds it satisfactory for all kinds of material. With a view to hastening the process, many modifications have been suggested. This speeding up can be brought about by increasing the boiling point of the sulphuric acid with salts or by introducing a catalyst. In the first case, the higher the temperature, the more rapid the oxidation, whilst in the second case the process is accelerated by substances capable of existing in two states of oxidation.

Although these modifications can sometimes hasten the action of the acid, the final results are not always obtained in a shorter time. Thus, Dr. Treadwell in his recent work, in describing the Willfarth modification of the Kjeldahl process (the use of mercury) recommends boiling for two or three hours. Experiments by the author show that in leather analysis, one hour's heating is quite sufficient if permanganate is used with the acid.

The higher the temperature, and the more concentrated the sulphuric acid, the more rapid is its action on leather. Besides, heat and sulphuric acid act quite as well as any oxidizing agent, since sulphuric anhydride is formed. To avoid loss of nitrogen, it is better that the disintegration of the acid should follow the other process, hence the temperature should only be gradually raised in Kjeldahling. Van Engelen, of Brussels University, has recommended the use of a small amount of sugar, which facilitates the action of the acid on very complex and highly polymerized organic material. The author thinks that the acid and sugar gives rise to free molecules of water, which depolymerize the complex bodies and so facilitate the action of the acid.

* *Collegium*, London Edition, in French in the January and February issues. This abstract by D. Woodroffe, pp. 43-5 in February issue.

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Experiments have been carried out at Liege using various modifications.

	Per cent. N	Per cent. H.S.
1. Potassium permanganate	10.06	56.64
2. Anhydrous copper sulphate (0.02 gr.) and permanganate	10.04	56.42
3. Anhydrous copper sulphate alone (0.02 gr.)	9.60	53.95
4. Mercury and sodium sulphide after dilution	9.64	54.10

In these experiments, 0.7 gram of ground leather was soaked with 10 cc. of strongest commercial sulphuric acid. In the fourth experiment, conducted according to Willfarth (*Chem. Zeit.* 9, 502) a few cubic centimeters of sodium sulphide solution are added before distilling and after adding the alkali. The above figures show that under the above conditions, the best accelerator is permanganate. Professor Procters' modification (*J. S. C. I.*, 2, XIX, 1900) using anhydrous copper sulphate is quite good if the action is finished with a few crystals of permanganate. Without the latter, sufficiently high results are not obtained unless more acid is used, and the time of heating is doubled. In our experiments, as in those of Professor Procter, the use of mercury has given slightly lower results, and still lower, as one reduces the time of heating.

2. *Length of Reaction with Concentrated Sulphuric Acid.*—Van Engelen has shown that the action of the acid in Kjeldahling oil cakes is greatly hindered by the presence of oil. The author does not think this applies to leather analysis, in fact, it is not necessary to conduct the Kjeldahl operation on the original material but on the leather after fat extraction and removal of uncombined tan.

	Per cent. N.	Per cent. H.S.
One-hour	10.00	56.54
Half-hour	10.06	56.54
Quarter-hour	9.96	55.98
Three-hours	10.04	56.42

It is evident that half-an-hour is quite sufficient for the heating. After the action the liquid was quite limpid, wine-red in color, which varies according to the mode of tannage of the leather.

3. *Minimum Quantity of Sulphuric Acid to be Used.*—Con-

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centrated sulphuric acid is quite powerful enough; there is no need to use fuming acid.

C.C. acid used	Per cent. N.	Per cent. H.S.	
10 cc.	10.04	56.42	0.7 gr.
15 cc.	9.96	55.98	Leather
20 cc.	9.92	55.75	used.

It is thus useless to use more than 10 cc. acid since excess only involves the use of more alkali and consequent bumping of the liquor in the distillation process. Fifteen cc. is better to soak the leather with; 10 cc. should be used to soak the leather and 5 cc. to carry down particles on the side of the flask. A glass bead should be put in to prevent bumping, the flask should be heated over wire gauze in an inclined position. The Kjeldahl flask used was of 250 cc. capacity, oval in shape, of hard glass. At the finish of the acid reaction the contents of the flask were poured into 100 cc. of cold water contained in an ordinary liter flask. The Kjeldahl flask was washed out two or three times, and the washings added to the liter flask. The author prefers this method to distilling from the flask in which the Kjeldahling has been done, since that flask is too small and a larger one is very liable to break.

Finely powdered permanganate when added to hot sulphuric acid, is instantaneously decomposed into the anhydride, and oxygen is violently emitted from the surface with a bright glow which may give place to a slight explosion. By the action of organic matter, the liquid is very much diluted, and to complete the reaction it is necessary to add large quantities of permanganate, with continual shaking. The result of this is the presence of a large amount of manganous salts which precipitate in the distillation process and cause much annoyance. The permanganate must therefore be added in the cold. Cool the flask and contents to about 50° C., add twelve crystals of permanganate and then gradually increase the temperature.

	Per cent. N.	Per cent. H.S.
Analysis continued as soon as colorless	10.06	56.54
Boiled quarter-hour after colorless	10.04	56.4
Boiled half-hour after colorless	10.04	56.4

Sometimes mere shaking will cause complete decoloration, but usually the liquid must be heated to boiling. The table shows

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that there is no need to prolong the heating after the liquid has lost its color.

As regards the distillation, the author recommends the introduction of the caustic soda into the flask, through a stoppered funnel, so as to prevent loss of ammonia. A large excess should not be used as there is danger of its being carried over into the receiver; besides the ammonia is less readily evolved in that case also. For regulating the boiling he proposes powdered zinc as it is quite efficient and any danger of reduction of other nitrogen compounds which may be present in the acid and alkali, can be counteracted by doing a blank determination with these two. The author does not favor the use of intricate devices for catching spray. He suggests a long, wide bore tube bent twice at 140 deg. with the end in the distilling flask, fluted to facilitate the dropping of the condensed vapor. A few glass beads should be fixed in that part of the tube so that the vapor has to pass through small openings. It then comes out into the wide tube with more force, causing total condensation of the spray particles.

This method if carried out as above described gives exact and concordant results with a maximum of ease and rapidity.

POTASSIUM CYANIDE AS A QUALITATIVE REAGENT FOR TANNING MATERIALS.*

By Hugh Garner Bennett, M.Sc.

Potassium cyanide has been previously suggested as a qualitative reagent for tanning materials, for two purposes, *viz.*, as a test for Lentisco (*Pistacia lentiscus*), and as a test for gallic acid. The author's purpose in this article is to discuss these tests and also to suggest a new use for potassium cyanide as a reagent for distinguishing pyrogallol from catechol tannins.

1. As a test for lentisco, potassium cyanide was suggested by Andreasch, whose object was to detect this material when mixed in with sumac. Procter, however, reports unfavorably upon this test and suggests the bromine test as a much better alternative. Potassium cyanide certainly gives a decided precipitate

* *Collegium*, London Edition, Feb., 1915, pp. 56-60.

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with a fresh solution of lentisco, but in the writer's experience sumac invariably gives a similar precipitate! Both these precipitates are yellow and flocculent, and apparently indistinguishable. None of the other common commercial tanning materials yield such a precipitate, so that if potassium cyanide is of any use in this way it is rather to distinguish lentisco and sumac from other tanning materials.

The working of this test evidently depends upon the fact that potassium cyanide is hydrolyzed in aqueous solution, and yields ionized caustic potash and unionized hydrocyanic acid. The yellow precipitates are caused by the alkali, and it is not surprising, therefore, that the pure caustic alkalies, caustic potash and caustic soda give the same effects as cyanide. They are also pleasanter, safer and more convenient reagents. If caustic soda be added to other infusions of tanning materials, *e. g.*, valonia, chestnut, etc., it tends to clear them rather than to give a precipitate on account of its solvent effect on the ordinary insoluble matters, such as bloom.

It is conceivable that the results of Andreasch may be explained from the possible differences caused by the relative concentration of the solutions and of the reagents. There may thus be dilutions at which lentisco gives a precipitate and sumac does not, though the writer has not found them. This view, however, receives some support from the fact that concentrated gallotannic acid and 10 per cent. potassium cyanide will give a precipitate, whereas a dilute solution of the former will not.

The yellow color of the lentisco and sumac precipitates suggests that the associated coloring matters may be the cause of the precipitate, but against this view is the fact that no such precipitate is obtained with a myrobalans infusion.

2. Solutions of pyrogallol, gallic acid, and gallotannic acid, when shaken in a test tube after adding a solution of potassium cyanide, show a bright red color, which soon fades, but which returns on shaking. This is an exceedingly useful and delicate test for the above substances. The reaction is evidently due to the pyrogallol grouping $= C_6(OH)_3$ (1 : 2 : 3) and the cyanide again functions as an alkali for the reason mentioned above. The reaction is clearly one of direct but unstable oxidation. As

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is well known, pyrogallol undergoes rapid oxidation in alkaline solution, absorbing oxygen with great avidity. In this instance the alkali is of a milder nature and the oxidation thereby retarded to a definite and unstable stage. In the case of gallic acid the progress of the normal pyrogallol-alkali oxidation is still further arrested by the carboxyl group (—CO OH) in the molecule, and the internal structure of gallotannic acid acts also in the same sense. Hence, caustic soda, caustic potash and ammonia give with gallic acid precisely the same reaction as potassium cyanide, the OH^1 ion being the effective agent.

The reaction may be intensified in various ways, such as the following:

1. The shaken mixture is poured into excess of aerated water.
2. A little hydrogen peroxide is added before the cyanide solution.
3. The mixture is aerated more thoroughly by shaking in a stoppered bottle.
4. The mixture is exposed to air by being spread out in a shallow porcelain vessel.

In the case of pyrogallol itself the oxidation is too rapid with caustic alkalies to show this red color, the mixed solutions rapidly becoming dark brown and black.

It is a curious fact in the case of gallic acid, that if still milder alkalies are employed, the oxidation is taken to a different stage—probably a further stage—and a green color is developed instead of a red. This effect is produced by sodium carbonate, potassium carbonate, sodium phosphate and sodium arsenate, these salts being all slightly hydrolyzed in aqueous solution to ionized caustic alkali and unionized acid. This oxidation is also slower than the "red" oxidation and shows best when the mixed solutions are allowed to stand for an hour or two exposed to air. When a solution of ammonium carbonate is added to gallic acid the two stages can both be observed, first the red color shows, and then the green. A similar effect may be obtained by adding to gallic acid first a very little caustic soda and then a larger amount of sodium carbonate.

It is interesting to compare this behavior of pyrogallol and its

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derivative gallic acid, with the behavior of catechol and its derivatives, protocatechuic acid and catechin, towards the same reagents. In the case of catechol the susceptibility to oxidation in alkaline solution is not so great as with pyrogallol, owing doubtless to the absence of one hydroxyl group. In this case therefore it is the "green" stage of oxidation which is unstable, and the "red" stage is stable. When caustic soda is shaken with catechol the green color develops, but when the shaking stops the color quickly changes to red. If again shaken the green color reappears, and again changes to red when allowed to stand. This may be repeated a number of times, both colors becoming stronger and eventually darker. Caustic potash and ammonia react similarly, but cyanide does not react. When caustic alkalies are added to catechol without shaking the green color shows first, doubtless on account of dissolved air, but it quickly fades to a pink. The alkaline carbonates give no color at first but develop green on shaking vigorously, which color quickly changes to red as usual. Sodium arsenate does not react readily, but the red color develops if the mixture be allowed to stand overnight.

In the case of protocatechuic acid the oxidation is still further limited, not only on account of there being only two phenolic groups, but also because of the inhibiting effect of the carboxyl group—as in the case of gallic acid. In this case ammonia, sodium carbonate and other of the milder alkalies produce no color at all, while caustic soda produces only the red color, even with vigorous shaking. Sodium arsenate produces a faint red when allowed to act over night.

Catechin behaves very similarly to prototechuic acid, but contains no carboxyl group and is,—perhaps in consequence—more susceptible to the "red oxidation" than protocatechuic acid. Catechin yields the red color with caustic soda, and also feebly with ammonia. It also gives the red color with the still feebler alkalies such as sodium arsenate, being indeed more prone to this than catechol itself. The author, however, has not obtained the "green oxidation" with any reagent.

To summarize the facts, we must note that both the pyrogallol and catechol groups are susceptible to these two types of oxida-

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tion, but that the result is influenced both by the nature of the alkali and the nature of other attachments to the benzene ring.

Some practical use may be made of these facts. The author has tried to differentiate between pyrogallol and catechol tannins by means of these alkaline oxidations. In the case of caustic soda and potassium cyanide the experiments were in vain. Both pyrogallol and catechol tans give the "red oxidation," though the former certainly give it more strongly. Still all tans develop on shaking a reddish color. The catechol tans and non-tans will hardly yield the "red," and the pyrogallol tans will yield the "red" but not the "green."

With the milder alkalies, however, the infusions of catechol tans show on standing the red color, while infusions of the pyrogallol tans develop the green color. This apparently is the explanation of the "sodium arsenate test" recently suggested by the author. The tan infusions are diluted until they no longer color the water very distinctly, sodium arsenate solution is added, and the mixture allowed to stand an hour or two. The pyrogallol tans all have associated with them gallic acid and develop a green color; the catechol tans have associated the catechins which yield a red color. The colors develop at the surface of the solution. The mixed tannins yield sometimes gallic acid, sometimes catechin, and may therefore be subdivided into two sections according to which of these typical non-tans is present or in predominance. Thus mimosa bark and oak bark yield the red color, whilst lentisco and babla develop the green.

It should be noted that it does not seriously matter if any tanning material contains *both* gallic acid and catechin, for red and green are complementary colors, and in mixture produce black. One of these non-tans will almost certainly be in excess of the other, so that either red or green is always shown. Thus oak bark, which is known to yield gallic acid, has in a fresh infusion a much greater amount of catechin, so that the red color is developed.

In two cases the action of potassium cyanide is specially noteworthy. An infusion of babla gives the red color at once and develops it very strongly on shaking. This seems to indicate that this material yields a comparatively large amount of gallic acid

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even to a fresh infusion. The other case is that of algarobilla, in which the pyrogallol grouping is singularly liable to rapid oxidation. On adding potassium cyanide to a fresh infusion of algarobilla the mixture darkens almost as rapidly as pyrogallol. The conclusion seems to be that either the pyrogallol group in the tannin molecule is very susceptible, or that the material contains an oxidizing agent. In either case the practical importance of this point is obvious. Algarobilla might have greater commercial value if leached, reduced, and made into an extract.

In conclusion of this section it may be noted that these alkaline oxidations may be conveniently seen and compared, if the ordinary "non-tan filtrates" obtained in the ordinary course of analyses be employed, especially those obtained in the revised shake method recently suggested by the author, on account of the greater amount of the astringent non-tannins so obtained.

3. Potassium cyanide may be employed to distinguish the pyrogallol and catechol tans in the following way. An excess of 10 per cent. cyanide solution is added to a clear infusion of the tanning material and the mixture poured into an excess of hard water. All the pyrogallol tans and some of the mixed tans develop a very distinct precipitate. Other tanning materials of the catechol class do not give this precipitate. The amount of precipitate does not of course appear large on account of the large dilution made in the course of the test, but the presence or absence of the precipitate is easy to observe.

Pyrogallol itself does not give any precipitate, and some of the mixed tans (*e. g.*, mimosa bark) which answer many tests for pyrogallol, do not give any precipitate, but the precipitate is obtained from all those tanning materials which give a green color with the sodium arsenate test, *i. e.*, by all those materials which contain gallic acid in a freshly made infusion. Gallic acid itself, however, yields a negative result, so that the reaction is obtained apparently from all those tannins with which gallic acid is usually associated.

The mechanism of the reaction is rather obscure, but is evidently connected with the calcium salts of the hard water. Distilled water does not work the test. The water used contains 25 parts chalk per 100,000, and very little permanent hardness.

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The author has found the test to work with a very dilute solution of calcium chloride, containing 50 parts $CaCl_2 6H_2O$ per 100,000. Strong solutions of calcium or magnesium chloride yield a precipitate with all tanning materials.

An infusion of algarobilla does not usually yield a precipitate on account of its exceedingly rapid oxidation in alkaline solution, as noted above. A dark liquid is obtained instead. A precipitate may be sometimes obtained, temporarily, if the test be carried out very quickly. Many materials develop a purple color also, of varying intensity.

The author's thanks are due to Professor H. R. Procter, D.Sc., for his kindness in supplying a quantity or catechin, and of protocatechuic acid.

ABSTRACTS.

The Warble-fly. G. S. CARPENTER and others. *L. T. R.*, Feb. 17, 1915. This article is taken from a report of experiments and observations on the warble-fly previously published in the JOURNAL of the Department of Agriculture and Technical Instruction for Ireland.

Of the various results obtained the most important is the fact, indicated both by the muzzling experiments and by direct observation, that this first-stage maggot bores into the host-animal directly through the skin, as was generally believed to be the case until the discovery of second-stage larvæ in the gullet led to the view, widely held recently, that the mode of entrance is by way of the mouth.

During the last two springs at Ballyhaise as the warble maggots were extracted they were carefully examined and the species determined as far as possible. The warbles were extracted and two different counts taken in April and May at dates dependent upon the time of "ripening." The following tables give the numbers of the fourth-stage maggots of each species at the different counts. In the third larval stage the species cannot be determined, as both *Hypoderma bovis* and *H. lineatum* are then apparently alike, though the armature of the cuticle differs distinctly from those of the fully grown or fourth-stage maggots.

TABLE 1.—1913.

Species of Warble maggot	1st count, April 15th	2nd count, May 7th	Total identified
Hypoderma lineatum	580	11	591
Hypoderma bovis	237	469	706
Third stage	81	44	125

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TABLE II.—1914.

Species of Warble maggot	1st count, April 27th	2nd count, May 11th	Total identified
Hypoderma lineatum	144	11	155
Hypoderma bovis	378	476	854
Third stage	47	39	86

These figures fall far short of the total number of maggots that were in the animals, as very many were destroyed in the operation of extraction and could not be identified. *Hypoderma lineatum* is clearly the earlier fly, and there was a great reduction in the number of maggots of this species last spring as compared with the previous year.

For the purpose of trapping the maggots as they emerged, four animals were kept tied up for about a month in the spring of 1913, and this year four others were tied up for the same purpose. The maggots were caught in small zinc or wire traps, like those described in the first report of this series. When the maggot is ready to emerge it is almost black and the breathing hole is large; this is the time to put on the cage. The maggots always emerge very early in the morning and in good weather. In this way, during the spring of 1913, 35 maggots were captured; three were identified as *Hypoderma lineatum* and the others as *H. bovis*. The maggots were put, immediately after they had emerged, into boxes in which were placed sods of earth, and which were covered with wire gauze; they were kept in the open in all weathers to ensure natural conditions. Two *lineatum* and 23 *bovis* flies emerged, confirming in every case the identifications already made on the larvæ. Flies had developed in the other puparia but had perished; about half the flies were males and half females. The specimens of both species passed about eight weeks in the pupal stage. This last spring (1914) 35 maggots were obtained in the same way, six *lineatum* and 29 *bovis*. No *lineatum* flies emerged although they developed in the puparia, but 25 *bovis* flies were successfully reared, 15 males and 10 females. The flies emerge very early on bright sunny mornings.

As the calves were confined in a pen we had a good opportunity of watching the fly at work egg-laying during both summers. The fly almost exclusively lays its egg on the legs, not confining itself to any particular part, but showing a decided preference—at least, as regards *Hypoderma bovis*—for the heel or hock-joint of the hind limbs. We saw the flies strike the calf a few times on the side and very often on the flanks and hips, but never on the back. The fly works very quickly, but only for a few minutes at a time. *H. lineatum* lays her eggs on the hairs in rows, and must therefore cling on for a few minutes while laying them. *Hypoderma bovis*, however, lays her eggs singly and quickly, and the animals get very excited; it has been observed by Gläser that *H. bovis* annoys the animals more than *H. lineatum*, the difference being probably due to the method of egg-laying, but we cannot confirm the statement, as we have never had an opportunity of watching the latter fly at work. At Athenry, however, our attention was called to eggs of *H. lineatum* laid

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in numbers on the hairs of cows' thighs, not far below the root of the tail. As the hairy covering in this region is short and scanty, good opportunity was thus afforded for observation.

One day while we were watching the calves at Ballyhaise, as they were crowded in a corner of the pen, one of us happened to touch a calf lightly on the leg with the point of a stick; the animal kicked violently and got excited. This led us to repeat the experiment, touching different parts of the body; we found that the calves became annoyed and excited and commenced to gad if touched on any part of the legs or flanks, but they did not stir if touched on their backs. This led us to conclude that the mere irritation caused by the fly touching the calf in its persistent attacks is enough to cause the animals' gadding and terror; they cannot get rid of the fly unless they plunge into a river, or find shady shelter. The calves might be supposed to have a natural instinct that the fly is their enemy, because they gad the very first moment it attacks them and they do not seem to mind the dozens of other flies, some of which are blood-sucking; the common "Clegs" (*Haematopota*), for example, which abound at Ballyhaise, excite the animals simply to shake the skin. Very few eggs can be obtained by examining a calf's legs, but by putting a captured fly "sleeved" in a wire gauze cage on a calf's back or side, she will lay sometimes, not always, quite a number of eggs. We could not always be sure of thus obtaining them, but this seems to be the only way of getting a satisfactory number of eggs to work with.

Last summer we observed that the eggs laid by *Hypoderma bovis* on the calf which we were watching changed in color on the fourth day after being laid. We found when we took them off and examined them more closely that they were empty shells split open at the apex. The next time eggs were found on the calf some were taken off every day, examined and put into an incubator at body temperature. On the third day the little maggots could be seen ready to hatch so we removed all the eggs and put them into the incubator; on the fourth day the eggs had hatched and on examining the slide seven little maggots were found. These were dead so it was not possible to use them for experimental purposes, but they provided material for a description of the outward structure of the first-stage larva.

Until the observations made in the summer of 1913 by Gläser in Germany, and by ourselves at Ballyhaise, the first-stage larva of a warble-fly had never been seen outside the egg. The so-called first-stage maggots mentioned by various writers as found in the gullets of cattle are really early second-stage larvæ. The newly hatched maggot, though only 0.8 mm. ($^1/_{30}$ in.) long, is distinguished by the relatively immense strength of its mouth-hooks, and of the spiny armature in transverse rows across its segments, especially on the ventral aspect. Between the strong mouth-hooks is a sharp spine directed forward; this is used for breaking through the egg-shell at hatching. The spines at the thickened tail-end of the maggot, in the neighborhood of the hinder spiracles or air-holes, are like

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strong hooks curved towards the dorsal region. The spines on the body-segments generally point backwards, so as to give the maggot a firm hold in the direction of its progress. The whole aspect of this little larva suggests that it could bore as readily through the skin as through the mucous coat of the gullet. That it does bore into the skin we are convinced as the result of the muzzling experiments and of the direct observations that we have been able to make.

During the summer of 1913 six calves were kept housed and never allowed out. To three of these were fed 16 newly-laid *Hypoderma bovis* eggs each; the other three were kept as "controls." The calves were never out until after the counts this spring (1914), and not one of them had any warbles. This result tells strongly against the view that the parasite gains entrance to the host's body by the eggs being licked in. There remains, however, the possibility that the young maggots might be licked in. Therefore, during this last summer (1914) six calves have been housed, and to three of these have been fed three newly-hatched maggots each of *Hypoderma bovis*. It was intended to feed a large number of maggots, but want of material prevented this. The other three have been kept as "controls," and none of them will be allowed out until after the maggot season next spring.

The presence of numerous eggs of *Hypoderma lineatum* on the thighs of cows at Athenry in June has been mentioned above. It will be observed by Mr. Lang the cattle herd there, that a few days after the eggs had been laid a soreness in the neighboring region of the skin with a discharge of matter appeared. On visiting Athenry we confirmed this valuable observation and the cows, standing quietly in the byre, proved better subjects for examination than restless calves in the field. On looking with a lens at the skin near the newly laid eggs we saw that it was perforated with minute holes from which flowed a watery discharge, hardening on the surface to form a scaly deposit. After a day or two the region became covered with small pimples, which disappeared a few days later. On squeezing the skin of the earliest "case" that could be obtained, some clear watery fluid exuded from the holes, and on examining a smear of this under the microscope we were delighted to find a newly hatched maggot of *H. lineatum*.

In July, 1914, we clipped a small patch on the shoulder of a black calf, and put seven maggots on it. They were very difficult to watch owing to the trouble of keeping the calf steady, and they were almost the color of the skin. Immediately they were put on the hairs they crawled down them to the skin, and directed their bodies perpendicular to its surface. We soon found that they were slowly disappearing into the skin. Four were lost sight of, but the other three were watched cutting into the epidermis with their mouth-hooks, and occasionally bending the hinder region of their bodies until they disappeared completely. It took them about six hours to get into the skin; possibly hair follicles may have facilitated entrance. Next morning there were three little eruptions or

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pimples just where they had entered, and we found four other little pimples indicating where the other maggots, which had been lost to view, had also bored in. On the calf from which the eggs had been taken we let about a dozen eggs remain on the hairs; these were taken off on the succeeding morning and found to be empty shells. The skin near these, when examined, exhibited a number of small pimples, easily seen with the naked eye, and resembling those observed on the cows at Athenry as already mentioned; they became a little larger during the day, and apparently burst during the following night, because next morning they were dried up and a small scab had been formed. We examined them, but found no trace of the maggots. In about a week all trace of the pimples was gone, not even a scar being left. The calf appeared to feel the maggot piercing the skin at first, because its restlessness made observation difficult, but the symptoms of discomfort soon passed away.

These observations confirm the belief deduced from the muzzling results that the maggot enters the animal's body through the skin and not by the mouth and gullet. As the eggs are laid on the lower parts of the animals, seldom, if ever, on the back, and as the maggots, according to our observations, enter the skin somewhat below the position of the eggs, it remains to consider by what course the parasite finds its way to the back.

Many farmers have complained that squeezing out the ripe maggots, as practiced for many years past at Ballyhaise, is too troublesome a method for use on a large scale in ordinary farm work. Attempts have, therefore, been made to find an effective dressing which may be used for maggot destruction. In the 1910 report a smear consisting of Archangel tar and paraffin was recommended, but subsequent experience has shown that this mixture, although it kills most of the maggots, has, in many cases, a highly injurious action on the cattle, making the skin very sore and destroying the hair. During the spring of the past two years, therefore, a number of applications have been tried in the hope that some might be found that would kill the maggots in the backs of the cattle without causing undue pain or suppuration, or injuring the appearance of the beasts. The results of this investigation have been, so far, disappointing. (Here follows a list of materials which have been tried. Most of them were useless. Others destroyed from 20 to 60 per cent. of the maggots, but the more efficient ones injured the skin. Good results were obtained with sulphur dioxide, but no suitable means of applying it have been discovered.)

Biochemical Synthesis of Glucosides and Polysaccharides. Reversibility of Enzym Reactions. E. BOURQUELOT. *J. Pharm. Chim.*, through *J. S. C. I.*, Feb. 27, 1915. The author has shown definitely that enzyms which hydrolyze glucosides or polysaccharides can reconstruct them from the products of hydrolysis. Aqueous and alcoholic solutions of dextrose contain the alpha and beta forms of this sugar in certain definite proportions,

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constituting an equilibrium mixture. If alpha glucosidase be added to an alcoholic solution, it attacks only the alpha dextrose, but as fast as this is converted into glucoside, there is a partial conversion of beta dextrose into the alpha form, and so the equilibrium is kept up. Each enzym is restricted in its action to compounds of the same chemical constitution and stereochemical structure. The equilibrium attained by enzym action in alcoholic solutions of sugars, like ordinary chemical equilibrium in solutions, is the result of two opposing reactions, hydrolysis and synthesis, proceeding at equal rates. The speed of each of these reactions varies with the concentration of the respective substances, so that the point of equilibrium is displaced if sugar is added to the solution, or removed by fermentation.

Determination of Nickel in Hydrogenated Oils. DR. FR. PRALL, Bremen. *Zeit. f. angew. Chemie,* 29 Jan., 1915, p. 40. The author's method for detecting nickel in hardened oils, previously published, is as follows: A few cc. of the fat are placed in a test-tube with an equal volume of concentrated HCl and warmed on a water-bath. The HCl solution is then filtered off and evaporated. The residue is moistened with a solution of dimethylglyoxime. Presence of nickel is shown by a red coloration. Sometimes this reaction is given by freshly expressed oils free from nickel, and sometimes special precautions are necessary to get the reaction when nickel is present. The author submits an improved method as follows: 100 to 200 grams of fat are ashed in a platinum dish, burning it down a little at a time. The ash is ignited strongly and then taken up in 3 to 5 cc. of water containing 5 to 10 drops of HCl, gently heated to remove most of the excess of HCl, and then excess of ammonia is added. The whole is allowed to stand some hours, when the iron and alumina are removed by filtration. The filtrate is transferred to a porcelain dish and evaporated to dryness. The residue is then moistened first with ammonia and then with alcoholic dimethylglyoxime solution. A red coloration results if nickel was present in the fat to the extent of 0.1 or even 0.01 milligram in 100 grams. L. B.

A Contribution to Shortening the Time of Tannage. By "S". *Ledertechn. Rundschau,* 1915 [7], 9-12. For military purposes only vegetable tanned leather is used and the manufacture still requires much time. No hastening of the process is permissible which wastes tannin or hide, or which lowers the quality of the leather for which military requirements are high.

Considering first the soaking, this should be confined to two waterings for the usual green salted hides. Small amounts of salt retained do not interfere in liming. Fresh, cool running water may be used in rinsing, but soaking in running water causes loss of hide substance. Soaking is more difficult with dried hides. Pure cold water should be used. While the addition of organic acids prevents putrefaction and also softens the

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hides by plumping, this last may go too far. Alkali is preferable (1 kg. NaOH per cubic meter) and if carried on to the limes assists these instead of requiring neutralization like acid. The alkali is added to the second water after the hides are partly softened. Old limes also soften, but at the expense of hide. The soaked hides should be brought into sound limes sharpened with sodium sulphide in order to loosen the hair quickly. The unhairing should be done very thoroughly and labor expended here counts later. Deliming is one of the most important factors in tanning, and should receive careful attention to secure a rapid tannage. If the hide is free from lime strong liquors may be used without fear. A bate for loosening the hide is generally superfluous. Dung bates reduce hide and are desirable only with glove leather and the like, or such as is sold by surface measure. Military leather may be made without the use of dung bate only by correct liming, complete deliming and correct tannage and currying. Such a leather will stand more fat than if loosened and weakened by a bate and moreover the hide can be tanned through in the time required for the fore-tannage of bated, incompletely delimed hide.

For the fore-tannage, a suitable tanstuff is used in sweet liquors. Upper leathers are tanned throughout in sweet liquor; vache and harness leather may be plumped in sour vats after the fore-tannage. When the grain has been slightly tanned in sweet liquor, it resists swelling in acids and there is no danger of brittle grain. Extracts only are used in quick tannage, principally oak, often quebracho combined with myrobalans, mimosa and chestnut. A substance rich in sugar, like pine, is desirable in order to maintain an acid content in which quebracho is deficient. Whether the tannage is carried out in vats or drums, the principle of gradual increase of tan content in the liquors is observed and with rationally delimed hides strong liquors may be used from the start. In many tanneries the preparation of the hide before tanning is still carried out too much on the lines adapted to the old process with bark and water.

W. J. K.

Cinchonine for the Detection of Sulphite-Cellulose in Leather. W. APPELIUS. *Ledertechn. Rundschau,* 1915 [7], 17. In order to make the test with the same certainty as with extracts, it is necessary to leach the leather as described below since deviations in the details may make the reaction uncertain as shown in a paper by R. Lauffmann (*Rundschau,* 1914, 877-80). There being no definite prescription for the extraction, he made a cold extract of the finely ground leather and found but a slight cinchonine reaction. The authors have extracted the same leather according to their method and obtained a decided reaction. It appears that leather containing sulphite-cellulose fails to give the reaction if extracted in a finely ground condition, either hot or cold.

Method.—5-10 grams leather are cut in little cubes and extracted hot with 100 cc. H_2O, boiling up once. (Leaching of the leather with dilute soda lye according to Dr. Moeller is not admissible with the cinchonine

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test.) After filtration, 5 cc. 25 per cent. HCl are added to the filtrate which is heated to boiling and filtered again. To 50 cc. of the filtrate, 20 cc. of cinchonine solution are added, and a very little tannin solution, the whole heated to boiling without moving the flask. In the presence of even slight amounts of sulphite-cellulose, the typical lumpy, brown black precipitate invariably appears and in copious amount. W. J. K.

PATENTS

Machine for Brushing Sole-leather. U. S. Patent 1,112,163. CARLETON RUHE, Olean, N. Y.

Method of Treating Leather. U. S. Patent 1,118,813. CARL E. SCHMIDT, Detroit, Mich. The leather is placed grain side down on a flat surface which is spread with adhesive substance, and worked out flat, remaining on the plane surface to dry.

Process for Leather-fiber Board. U. S. Patent 1,119,345. A. L. CLAPP, Braintree, Mass., assignor to Hide-Ite Leather Company, Boston. Scrap leather is treated with potassium bichromate and hydrochloric acid, and then beating it out in a bath of thiosulphate and hydrochloric acid.

Preparation for Preserving Leather. U. S. Patent 1,121,220. S. AGUILAR, New York. Caoutchouc, glue, enamel, turpentine, mixed.

Leather Staking Machine. U. S. Patent 1,130,769. FRANK F. SLOCOMB, Philadelphia, Pa.

Leather Substitute. U. S. Patent 1,130,619. R. A. MCLAURIN. Glasgow, Scotland. A web of fibrous material is dyed, coated with glue, and then coated on one face with nitrocellulose and camphor, and finally with pure nitrocellulose.

Leather-board. U. S. Patent 1,131,039. A. L. CLAPP, Braintree, Mass., assignor to Hide-Ite Leather Co., Boston. Chrome leather scrap is ground dry, and then beaten out with water and vegetable tanned leather scrap. Alum is then added.

Water-proof Chrome Leather. British Patent 21,998. J. L. ALLEN, Gloucester, England. Rosin, tallow, tar and paraffin dissolved in benzene.

Treatment of Skins. British Patent 23,841. E. D'HUART, Luxembourg. Skins which have been unhaired by means of barium or strontium hydroxide are treated with a glycerol ester or an alkali or alkaline earth salt of phosphoric acid to remove the depilatory.

Treating Hides with Brains and Smoke. British Patent 23,638. R. BROOKS, Goxhill, Lincolnshire. Hides are macerated in a mixture of brains and water boiled together, then staked, dried and smoked.

Extracting Tannin. British Patent 14,405. S. B. BILBROUGH, Johannesburg, South Africa. A soaking and squeezing process, involving several sets of rollers.

Tanning Materials. British Patents 18,258 and 18,259. J. Y. JOHNSON, London, for Badische Anilin und Soda Fabrik.

For tanning, water-soluble aromatic non-crystalline compounds are

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used, in which there is hydroxyl in the molecule, but not more than one hydroxyl group in each nucleus, in which two or more aromatic nuclei are combined in the molecule by one or more atomic groups or polyvalent atoms, and which contain one or more acid salt-forming groups in addition to the hydroxyl group. The compounds used have the property of precipitating gelatine, and are other than those described previously. The following examples are given: (1) Limed and bated hides are suspended in a solution of sulphonated dimethyldihydroxysulphobenzide, with the optional addition of a salt, such as common salt. A series of baths of increasing strength may be employed, and the suspension may be replaced by paddling or tumbling. After tanning, the butts are freed from acid, fatted, and dried. The tanning substance may be prepared by acting on dimethyldihydroxysulphobenzide (obtained by heating ortho-cresol with sulphuric acid) with fuming sulphuric acid until a water-soluble product is obtained which is poured on ice and freed from sulphuric acid by means of lime or baryta. (2) An aqueous solution of the product obtained by acting on sulphonated cresol with sulphur monochloride is used. The product is made by sulphonating cresol with concentrated sulphuric acid, cooling the mass, and pouring it slowly into sulphur monochloride. When hydrochloric acid is no longer evolved, the mass is poured on to ice, diluted, and boiled until the sulphur separates out. (3) Thionaphthol-sulphonic acid B, as described in German Specification 50,077, is used. (4) A neutralized reaction product of phenol, paraldehyde, and concentrated sulphuric acid is made into an aqueous tanning bath with common salt. (5) The neutralized product from phenol, sulphuric acid, and glycerin or products obtained by the action of glycerin on phenol-sulphonic acid are used. (6) Tanning is effected in a solution of the urea of 2-amino 5-naphthol 7-sulphonic acid. (7) Sulphuric acid is added to a mixture of phenol, glacial acetic acid, and grape sugar, and the resulting mass is dissolved in water and used for tanning after the excess of acid has been removed.

Extracts, Making and Treating.—Difficultly or insufficiently soluble tanning extracts are rendered more soluble by treatment with water-soluble aromatic sulphonic acids containing no phenolic hydroxy group, and also water-soluble non-crystalline aromatic compounds containing hydroxyl in the molecule, but not more than one hydroxyl group in each nucleus, in which two or more aromatic nuclei are combined by one or more atomic groups or polyvalent atoms, and in which there is one or more than one acid salt-forming group besides the hydroxyl group. These compounds are all capable of precipitating glue or gelatine. Two examples are given: (1) the product from heating together in specified conditions naphthalene, sulphuric acid, and formaldehyde is neutralized with caustic soda, and the resulting paste is added to a hot aqueous solution of solid quebracho extract; (2) solid quebracho extract is ground up and stirred into a warm concentrated solution of product No. (2), described above.

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Philip S. Tilden, 3500 Grays Ferry Road, Philadelphia, Pa.

In the April issue the names of Julian Alexander, Gilbert P. Smith and Alpheus E. White were given as elected to active membership. This was an error; the gentlemen are elected to associate membership. So was Mr. T. P. Black, whose name was wrongly given as J. S. Black.

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CHANGES OF ADDRESS.

V. H. Kadish, to % Milwaukee Patent Leather Co., Milwaukee, Wis.
Victor G. Lumbard, to 715 Judson Ave., Evanston, Ill.
Karl Schorlemmer, to Haltingen (Baden), Germany.
D. L. Tucker, to 312 W. Oley St., Reading, Pa.

DEATHS.

S. F. Macdonald, of Ashtabula, Ohio, an associate member of this Association.

R. Arnold Seymour-Jones, an active member of this Association. In reference to his death, the following letter was received by the Secretary:

PENDOWER, WREXHAM, 31st March, 1915.

DEAR SIR:—

I regret to have to inform you of the death in action in Flanders on the 27th instant of my brother, Richard Arnold Seymour-Jones, Lieutenant, 4th South Lancashire Regiment. He was a member of the American Leather Chemists Association. He was born in May, 1889, and was educated at Wellington College (Salop) and Leeds University, where he took B. Sc. (Hons.) and M. Sc. in Applied Chemistry of Leather Manufacture. He published a few papers in various journals and wrote under the pseudonym of "Heof Joppa" for the *Leather Trades' Review.* Two years ago he forsook the leather trade for the post of Physical Chemist at Messrs. Jos. Crosfield & Sons, Warrington. He had been the recipient of the Royal Humane Society certificate for an attempt to save a girl from drowning in 1912.

Yours truly,

The Secretary,
A. L. C. A.

(Signed) FRANK L. SEYMOUR-JONES.

TWELFTH ANNUAL MEETING.

The Twelfth Annual Meeting of the American Leather Chemists Association will be held at Atlantic City, N. J., May 27, 28 and 29, 1915. The committee in charge of arrangements for the meeting, has selected the Marlborough-Blenheim Hotel as headquarters, and a suitable room has been reserved for the meetings.

Persons desiring reservations are requested to apply directly to the hotel management, the rates being as follows:

European Plan—

1 room, 1 person, $3.00 and $4.00.
1 room and bath, 1 person, $4.00, $5.00 and $6.00.
1 room, 2 persons, $5.00 and $6.00.
1 room and bath, 2 persons, $6.00, $7.00 and $8.00.

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American Plan—
1 room, 1 person, $5.00 and $6.00.
1 room and bath, 1 person, $6.00, $7.00 and $8.00.
1 room, 2 persons, $9.00 and $10.00.
1 room and bath, 2 persons, $10.00, $11.00 and $12.00.

PROGRAM.

THURSDAY MORNING, MAY 27, 1915.

Opening Remarks by the President.....Dr. Louis E. Levi
Report of the Secretary-Treasurer.....H. C. Reed
Committee Report .....Lloyd Balderston
"Miscellaneous Methods."

THURSDAY AFTERNOON, MAY 27, 1915.

Address .....John Helfrich
"Chemical Control of the Beam-House."
Committee Report .....C. R. Oberfell
"Methods Dealing with Analysis in Connection with Beam-House Procedure."
Committee Report.....J. S. Rogers
"Free Sulphuric Acid in Leather."

FRIDAY MORNING, MAY 28, 1915.

Committee Report.....F. H. Small
"Filter Papers."
Committee Report.....T. A. Faust
"Moellons, Hard Greases and Hydrogenated Oils."
Address .....Lloyd Balderston
"Extraction of Valonia."
Committee Report.....A. C. Orthmann
"Detection and Estimation of Tanning Materials in Admixture."

FRIDAY AFTERNOON, MAY 28, 1915.

Address .....A. N. Dubois
"Coloring of Leather without the Use of Dyes."
Committee Report.....C. C. Smoot, III.
"Alundum Thimble in Water Extraction of Leather."
Committee Report.....F. P. Veitch
"Disposal of Tannery Waste."
Committee Report.....F. O. Sprague
"Official Method of Tannin Analysis."

SATURDAY MORNING, MAY 29, 1915.

Committee Report.....C. R. Oberfell
"Oils and Fats."
Election of Officers.
General Business.

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CONTRIBUTIONS OF THE CHEMIST TO THE LEATHER INDUSTRY.*

By W. H. Teas.

Although one of the most ancient of industries, and involving as it does chemical reactions, the leather industry has, in only comparatively recent years, received the attention of chemists. The record of the accomplishments of the chemist in this industry during the past twenty-five years will comprise most of the advance along chemical lines that has taken place in the industry. The advent of the chemist in the leather industry was induced by desire to effect economies in raw materials; research, and improvement in methods became a secondary effect of the chemist's presence in the tannery, but success in the primary effort for economy was responsible for secondary effects, and for the now very general custom of laboratory control of the tannery.

The leather industry is divided into general divisions of vegetable and mineral tannages, and each of these has been subdivided into many specialized industries developed by the product demanded, and the use of the raw material suited to the product. In general, the tanning agents used, the oils, greases, finishes, etc., have in themselves been the chemists' fields, and in these and in the methods of application the chemists have found their work.

The chemist has indicated improvements in the soaking and preliminary preparation of the raw skins, so that a saving of the costly hide substance has resulted; his work in selecting the proper depilating materials, and in improving methods of their application has resulted in economy and in improved products. Practically all of the progress in deliming hides by the use of special preparations has been accomplished by the chemist; and to him is also due full credit for the results of investigations of the influence of the character of the water supply on the tanning operations. The utilization of by-products in this preliminary stage of tanning is another branch of effort in which the chemist has demonstrated his value.

In vegetable tanning the chemist has improved the methods of

* Read at the New Orleans meeting, American Chemical Society, April, 1915. Reprinted from *J. Ind. & Eng. Chem.*, April, 1915, p. 283; *Hide & Leather*, April 3, 1915.

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leaching the raw tanning materials so that more of the tannic acid content has been made available; his laboratory work has shown the reasons for many of the rule-of-thumb methods of the practical tanner, and thereby afforded a means of anticipating and correcting conditions which would produce an unsatisfactory product. The standardization of tan-liquors, with the consequent tendency toward uniformity of product, could not have been accomplished without the work of the laboratory. The utilization of spent tan liquors formerly run to the sewer, by purifying and concentrating into a thick extract for mechanical tanning, is also a laboratory development; and the chemist is responsible for the progress so far made in the sewage disposal problems of the tanner.

The chemist has materially aided in the work of replacing the fast diminishing native barks, with combinations in proper proportions of foreign tanning materials, foreign and domestic extracts, so that physical characteristics and quality the leather produced under the new conditions is similar to the old product. The standardization of leather oils, greases and waxes, and the protection of the tanner against adulteration is a matter of course with any laboratory, but the standardization and protection was badly needed in the leather industry, and the accomplishment of the chemist in this line is fully credited. The development of special oils for leather work, especially sulphonated oils, and the application of the oils to remedy certain defects in leather, is due to the chemist; he is also responsible for special combinations of waxes and greases for stuffing leathers according to the requirements of the use to which the leather is put.

The development of the mineral tannages has been due almost entirely to the chemist; the chrome process was first suggested by a chemist and later its development to a commercial success was accomplished by a chemist. Ever since chromic tanning was started in a commercial way, the modifications of process and materials, tending to economy and improvement, have been due to chemists, so that one of the greatest accomplishments of the chemist in the leather industry has been the process by which most of the light leathers of the world are tanned. The successful lubrication of the fiber of chrome-tanned leather has meant

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much to the utility and consequent popularity of chrome leather, and by means of saponifiable and so-called "soluble oils" the chemist has materially helped in this important factor.

Other mineral tannages, and tannages by formaldehyde and other aldehydes, have been worked out by chemists and brought to more or less commercial success as a result of laboratory work. Combinations of mineral and vegetable tannages for the production of leathers for certain purposes, are also the work of the chemist. Synthetic tannins, or at least products which give reactions analogous to the natural tannins, have been introduced by chemists, and their commercial value in some lines of the industry has already been demonstrated.

In the manufacture of tanning extracts from raw materials which grow in localities distant from the tannery locations, chemists have played an important part. Clarification processes introduced by them have, in some instances, increased the availability of some tanning materials, which, without clarification, would have a diminished economic value. Credit is also due the chemist for the production of special extracts, which have made possible the saving of time and labor in the production of certain kinds of leather.

In the production of patent and enameled leathers, of fancy leathers, and in the field of dyeing and coloring so important to light leathers, and in the numerous other departments of tanning, not mechanical, which space will not permit of particularizing, the chemist has been and is an important factor in product improvement.

The chemist in the leather industry has had to overcome the prejudice of the practical tanner against tanning theory, and without guiding precedents has been obliged to make his own standards, and develop his own groundwork. Recognition of the value of the efforts of the chemists is evidenced in the vast increase in the number of tannery chemists during the past twenty-five years. And still further evidence is the establishment of a tanning school in which chemistry is the most featured branch in the curriculum; and also the definite plans for starting a national research laboratory to be supported by the industry, and to be devoted to research work in the chemistry of tanning.

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FOOT AND MOUTH DISEASE.

By John H. Yocum.

During the past fall and winter, a disease of cattle, sheep and swine, known as foot and mouth disease, has been prevalent over the central and eastern part of the United States; and up to the first of January, 1915, the Government reports state that there were killed 47,000 head of neat cattle, approximately 47,000 head of hogs, and about 7,000 head of sheep.

The Government allows that their payments in respect of this were in the neighborhood of $3,000,000, of which approximately one-half was for the cost of inspection, and the other half for the payment of the value of said cattle to the owners. This does not include the veterinary costs of inspection of the various States involved, nor their half of the killing values of the animals themselves, so that in the neighborhood of $6,000,000 from the outbreak of the disease in October to the first of January, has been used up in the methods adopted by the United States Government, and the various State veterinary departments.

This, of course, does not include the excess value of such animals as were held for breeding purposes, the value by the Government being determined for payment from the food value of the animal itself. As an instance of this, something like $3,000,000 worth of breeding value was represented by the cattle in the Dairy Show in Chicago in the latter part of October. These animals were to be slaughtered and paid for at their food value, but through pressure and otherwise, these said animals were relieved of the killing end and have been kept away, and are now probably as efficient for breeding purposes as they were before they were subjected to the possible contamination of foot and mouth disease.

One of the factors that must be borne in mind in this connection is that through Government control, animals that never showed a fever or probably never had foot and mouth disease, but were only associated with animals which did have this disease, were killed indiscriminately with the animals that were shown to have had this disease; so as a result, it is probable that more than one-half of the animals killed and destroyed did not

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have the disease, and probably would not have had the disease, had they been properly quarantined. It is well known that but a small proportion of the animals having the disease die from its effects. They do, however, lose about one year's growth and value.

No efficient methods of fumigation have been followed out, so that birds, mice, rats and other animals could be exterminated, which were in touch with infected animals and might have obtained this same disease and carried it from one locality to another.

In all likelihood, the destruction of approximately $3,000,000 worth of animals at the expense of approximately $3,000,000 worth of veterinary and other services, indicates a desire on the part of the Government and the States to conserve the animal industry; but owing to the fact that no effort has been made to reclaim or make salvage of the hides, nor of the fats contained in the animal, nor of the fertilizing values also held within the animals, it is evident that the tendency of the powers that be was to exterminate everything that was subject to contagion, and they had given no thought as to the conservation of the values probably obtainable by reasonable and efficient management of this infection.

Some of the veterinarians from Cornell have shown that animals infected with the foot and mouth disease are readily isolated, and can be brought back to a reasonable value within a year; that the methods pursued by the Governments in various States have been unnecessarily rigorous, and it is quite likely that the losses, both from cattle killed and certainly from the excessive number of veterinaries and inspectors paid for, are more than what was indicated in the report to Congress by the Department of Animal Industry. It would therefore follow that in all likelihood, between the loss of animals and the cost of inspection, the country has suffered a monetary cost of better than $12,000,000.

In view of the fact that one-half of this $12,000,000 has no doubt been spent for salaries, transportation and other costs of inspection, it is no more than fair to think that at least $6,000,000

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has been paid out for the actual loss of the animals and their possible value, even though infected.

In this connection it is worth while to realize that the hide from an animal valued at $60.00 (which might be the average of the neat cattle killed in the last 6 or 8 months on account of this disease), can be properly fumigated at a very slight cost, and would net in a general way, at least $15.00 per animal; that the horns, hoofs, heads and other bony tissues, as well as the remnants of the skeletons themselves, can be readily rectified into fertilizing material worth at least $28.00 per ton or in the neighborhood of $5.00 per animal; that the greases and other oils obtained through rectification of the carcasses would have amounted to at least $10.00 per animal; so that it is fair to conclude that one-half the loss occasioned by ignorant and destructive killing could have been avoided by the adoption of methods not impossible or indeed difficult.

As stated above, the hides from animals which are killed or have died from the foot and mouth disease can readily be disinfected and the transmission of the germ utterly prevented. In the treatment of the carcasses left, the usual procedure is to boil with a solution of sulphuric acid of about 10 per cent. It is acknowledged that the greases that are skimmed off the tanks in which the carcasses of these animals are disposed of can by no means carry the disease from which the animal died. It is further to be remembered that the carcasses themselves, after the grease has been extracted, are boiled down in the presence of sufficient sulphuric acid, to practically a dry mass. This dry mass is subjected to temperatures in the presence of excess sulphuric acid, which would absolutely prevent the life of spores or bacteria of even anthrax. This will sell for from $25.00 to $35.00 per ton as tankage, with a high percentage of ammonia and a considerable percentage of phosphoric acids, suitable for mixing with potash salts and other phosphates to make complete ammoniates or complete fertilizers for the farmer.

Pointing out these defects in the methods adopted by the Government, does not deny that the Government pursued what appeared to be, at the time, the most direct and efficient policies; but in that the same Government has thus destroyed values

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amounting to not $3,000,000, but to many millions more (considering the fact that many of the cattle killed were high grade and more valuable than their meat production), it is evident that the policy of conservation by the Bureau of Animal Industry has at least fallen down.

Much has been said of the general policy of conservation, but apparently no attempt has been made to conserve the valuable products resulting from the killing of cattle, sheep and hogs, because of the excitement and lack of poise of the officials therein interested.

It might be well for the liberal Government we have from time to time to investigate the possibilities of utilization of carcasses, before this condition arises; and no doubt were we living in Germany, the utilization of the necessary losses due to the extermination of any animal disease would have been figured out long before the necessity for this destruction occurred.

However, in the United States we have people who think that conservation is a panacea of all the evils, and that the Government should exercise it, but when these evils arise, we find that the Government through its various departments is not competent to rise to the occasion and exercise even common decency about the treatment of products, or exercise common sense about how far the necessity for total destruction goes.

Bearing in mind the shortage of hides in this country, and our consequent need of imported hides for the production of sufficient leather for our local purposes, the loss of 100,000 hides, worth one and one-half million dollars, is to be regarded with apprehension, even by people like myself, who are desirous of seeing the animal industry prosper and grow to its ultimate extent.

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REPORT OF 1915 COMMITTEE ON THE OFFICIAL METHOD OF TANNIN ANALYSIS.

By F. O. Sprague, Chairman.

The Council recommended for this year's work of this Committee that comparison be made between the rapid and slow cooling methods, using hide powder chromed over night, only. Four liquid extracts were suggested; ordinary quebracho, hemlock, myrobalans and oak. Presumably the idea was to use extracts of comparatively high insolubles in order to arive at the maximum difference between the two methods. Clarified quebracho has not generally been found to give as much difference between the slow and rapid cooling as ordinary. Mr. H. C. Reed kindly furnished the Chairman with a liquid quebracho, which, while not ordinary, yet had been found to give a marked difference. The results of some 37 analyses of this extract by 30 operators show such a difference between the slow and rapid cooling methods as to necessitate some action by this Association.

A glance at the averages shows that there is very little difference between the two methods, at least when using slowly chromed hide powder, in the total solids and non-tannins. This is generally conceded to be so. The hemlock and oak extracts show no difference in tannin. The myrobalans extract shows 0.20 per cent. higher tannin by the rapid cooling method and the quebracho shows 0.63 per cent. higher tannin by the rapid cooling. This is due in each case to lower insolubles by rapid cooling. Perhaps 0.63 per cent. difference will not look very high to some, when compared with the results of previous committees on dry quebrachos running over 70 per cent. tannin. But if it be considered that this is a difference of nearly 2 per cent. of the total tannin, and that the hemlock and oak extracts check very closely all the way through, as all should on an average of so many analyses as this, it will be seen that this is a very large difference. So large that it would seem that we should drop one or the other of the two methods, at least on quebracho and myrobalans.

Of the collaborators who mention any preference for one or the other of the methods, the following might be mentioned: two find not much difference; two find a difference; four prefer the

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slow cooling; one finds greater uniformity by slow cooling; and one finds greater uniformity by the rapid cooling and believes the slow cooling should be eliminated. It should be noted here, that others have expressed a preference for the rapid cooling in previous years.

In the report of the Committee on Revision of Methods, this JOURNAL, 1912, p. 290, it is stated that the results of the 1910 Committee on Rapid Cooling of Tan Solutions and on Filtration (Asbestos-Kaolin Method), this JOURNAL, 1910, p. 513, show greater uniformity in the rapid cooling method. The maximum difference in insolubles is made use of here, and is the lowest result subtracted from the highest. This has been used in other reports, and is noted in these tables, but does not show much to the writer. If the law of averages means anything, why consider only the two results furthest from the average in estimating the general agreement of results? Why not consider each result? In Table 6 I have shown the deviation of each result from the mean, and the average deviation. This is on the tannin only, of each extract by slow and by rapid cooling. Lack of time, only, prevents this estimation on the other results. The average deviation shows, on the whole, much greater concordance in the slow cooling method, especially on the quebracho, and is, to my mind, the only way it can be estimated. It is interesting also, as showing the relative agreement of the different extracts, the slow cooled oak giving the greatest concordance, and the hemlock the widest variation.

The Chairman wishes to thank all those who have collaborated on these analyses, and also Jno. H. Heald & Co. inc., J. S. Young & Co., and Mr. H. C. Reed, for the samples.

COMMENT BY COLLABORATORS.

ROY H. WISDOM: *Quebracho Extract.*—The extract submitted gave a solution of colloidal character, markedly so in the rapidly cooled one. This condition made it extremely difficult to secure an absolutely clear filtrate and in fact impossible in a working day, on the rapidly cooled solution. *Chestnut Oak Bark Extract.*—The differences here shown are all within the limit of personal error and apparently either method is applicable.

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Hemlock Extract.—Here again a difference is noticeable and no doubt due to the methods. *Myrobalan Extract.*—Same remarks as applied to hemlock. *Summary.*—So much work has been done along this line, especially on ordinary and partly clarified quebracho extracts, and the majority confirming the conclusion that on this extract at least, a marked difference is shown by the two methods, that it seems a waste of time to continue further work in proving what we already know. In fact, the writer made some notes on the comparative analysis report which were published in the April, 1914, JOURNAL, and later proposed a change in the method which was published in the June, 1914, JOURNAL, and bearing directly on this subject. What disposition has been made by the council of this proposed change is at the present writing unknown to the writer. The fact remains, however, that as long as the two methods remain optional in all cases, we are bound to get results at greater variance than if the restrictions were more limited.

T. S. DUNNIGAN: I find the greatest difference was in the insolubles of the quebracho extract, showing a difference of 0.42 per cent., while in the hemlock sample there was a difference of 0.07 per cent. This is contrary to my expectations, as the writer has generally found that an extract containing a large percentage of insolubles, such as unclarified hemlock or ordinary quebracho, generally shows the greatest difference in the two methods and invariably gives a greater percentage of insolubles by the rapid cooling method. There is not much difference shown in the tannins; the chestnut oak showing only 0.15 per cent., the quebracho 0.13 per cent., myrobalans 0.07 per cent., while the hemlock showed the same, making a difference of only 0.09 per cent., for an average of the four samples, which is as close as can be expected.

W. K. ALSOP: You will note that the slowly cooled solutions tend to show more insolubles than the rapidly cooled in 3 of these samples. This is most marked in the sample of quebracho. I do not know that I have any other comments to make, except that the difference between the rapidly and slowly cooled solutions seems to be more marked and consistent than in some other work we have done.

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TABLE I.—TOTAL SOLIDS PER CENT.

No.	Analyst	Quebracho extract			Hemlock extract			Myrobalans extract			Chestnut oak bark extract			No.
		Slow	Rapid	Difference	Slow	Rapid	Difference	Slow	Rapid	Difference	Slow	Rapid	Difference	
1	Roy H. Wisdom	45.52	45.60	+0.08	43.09	43.16	+0.07	41.53	41.51	—0.02	45.64	45.72	+0.08	1
2	T. S. Dunnigan	45.41	45.41	0.00	43.13	43.20	+0.07	41.48	41.60	+0.12	45.66	45.66	0.00	2
3	W. K. Alsop and J. E. McNutt	45.65	45.5	—0.15	42.95	42.85	—0.10	41.4	41.45	+0.05	45.7	45.8	+0.1	3
4	W. K. Alsop and E. R. Lobaugh . . .	45.6	45.65	+0.05	42.85	42.75	—0.10	41.6	41.4	—0.2	45.6	45.6	0.0	4
5	C. C. Smoot, III and L. E. Stacy, Jr.	45.50 45.49	46.00 45.74	+0.50 +0.25	42.80 42.83	42.92 42.99	+0.12 +0.16	41.04 41.09	41.42 41.43	+0.38 +0.34	45.70 45.59	45.91 45.79	+0.21 +0.20	5
6	F. P. Veitch, J. S. Rogers and R. W. Frey	45.35	45.32	—0.03	42.82	42.91	+0.09	41.32	41.48	+0.16	45.66	45.65	—0.01	6
7	F. A. Hayes	45.05 44.94	45.14 45.10	+0.09 +0.16	42.53 42.37	42.37 42.22	—0.16 —0.15	40.35 40.35	40.53 40.90	+0.18 +0.55	44.57 44.76	44.96 45.05	+0.39 +0.29	7
8	F. O. Sprague and H. J. Newman	45.98	45.72	—0.26	43.05	43.03	—0.02	41.75	41.61	—0.14	45.52	45.72	+0.20	8
9	H. A. Helder	45.33 45.22	45.14 44.57	—0.19 +0.35	42.54 42.58	42.88 42.88	+0.34 +0.30	41.67 41.67	41.55 41.55	—0.12 —0.12	45.89 45.99	45.87 45.82	—0.02 —0.17	9
10	W. A. Fox	46.00	46.01	+0.01	43.19	43.18	—0.01	41.73	41.70	—0.03	46.09	45.96	—0.13	10
11	H. C. Reed and Geo. W. Toms, Jr. . .	45.37	45.48	+0.11	42.83	42.84	+0.01	41.43	41.44	+0.01	45.94	45.89	—0.05	11
12	C. W. Norris and Adolf Schubert . . .	45.47	45.58	+0.11	42.94	42.91	—0.03	41.56	41.66	+0.10	45.91	46.03	+0.12	12
13	J. M. Seltzer	45.65	45.59	—0.06	42.94	43.01	+0.07	41.64	41.59	—0.05	45.71	45.76	+0.05	13
14	Frank F. Marshall . .	45.46	45.57	+0.11	42.86	42.95	+0.09	41.29	41.41	+0.12	45.63	45.68	+0.05	14

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15	T. S. Greaves	45.47 45.49	45.48 45.50	+0.01 +0.01	42.98 43.06	43.02 43.14	+0.04 +0.08	41.22 41.37	41.34 41.24	+0.12 —0.13	45.74 45.76	45.73 45.78	—0.01 +0.02	15
16	C. Eachus	45.97	45.83	—0.14	43.14	43.16	+0.02	41.75	41.62	—0.13	—	—	—	16
17	F. M. Loveland	45.40	45.44	+0.04	42.85	42.65	—0.20	41.37	41.13	—0.24	45.50	45.44	—0.06	17
18	P. M. Randall	45.81	45.30	—0.51	43.29	42.65	—0.64	41.09	41.62	+0.53	46.35	45.71	—0.64	18
19	Thos. A. Faust	45.95 46.04	46.10 45.94	+0.15 —0.10	43 01 43.07	42.91 43.00	—0.10 —0.07	41.36 41.51	41.34 41.48	—0.02 —0.03	45.66 45.85	45.74 —	+0.08 —	19
20	Oskar Riethof	—	—	—	43.16	43.17	+0 01	41.69	41.76	+0.07	46.04	45.96	—0.08	20
21	R. J. Bailey	45.34	45.63	+0.29	42.89	42.91	+0.02	41.36	41.37	+0.01	45.61	45.70	+0.09	21
22	H. L. Pierson	45.66	45.63	—0.03	42 92	43.14	+0.22	41.76	41.70	—0.06	45.85	45.83	—0.02	22
23	Chas. R. Oberfell and F. M. Richeson . . .	45.50	45.47	—0.03	42.80	42.81	+0 01	41.62	41.64	+0.02	45.80	45.68	—0.12	23
24	F. H. Small and V. J. Mlejnek	45.63 45.52	45 57 45.49	—0.06 —0.03	42.84 42.99	42.74 42.84	—0 10 —0.15	41.53 41.40	41.43 41.41	—0.10 +0.01	45.67 45.71	45.76 45.71	+0.09 0.0	24
25	Thos. J. Mosser	45.68 45.67	45.73 —	+0.05 —	42.76 42.76	42.70 42.73	—0.06 —0.03	40.86 40.72	40.72 40.78	—0.14 +0.06	45.23 45.44	45.17 44.96	—0.06 —0.48	25
26	E. A. Wallin	45.55	45.58	+0.03	42 99	42.81	—0.18	41.50	41.55	+0.05	45.83	45.82	—0.01	26
27	W. S. Loud	46.08	45.83	—0.25	43.16	42.93	—0.23	42.20	41.95	—0.25	46.48	46.34	—0.14	27
28	Theodor Veit	45.69	45.69	0.00	42.80	42.80	+0.06	41.22	41.18	—0.04	45.69	45.61	—0.08	28
29	R. E. Porter	46.10	46.05	—0.05	42.58	42.86	+0 28	42.45	41.70	—0.75	46.03	45.95	—0.08	29
30	E. R. Olds	46.02	46.17	+0.15	43.10	43.10	0.0	41.76	41.94	+0.18	45.94	46.12	+0.18	30
	Average	45.58	45 59	+0.01	42.89	42.88	—0.01	41.42	41.42	0.00	45.71	45.70	—0.01	
	Highest	46.10	46.17	{+0.50 —0.51	43.29	43.20	{+0.34 —0.64	42.45	41.95	{+0.55 —0.24	46.48	46.34	{+0.39 —0.64	
	Lowest	44 94	44.57	0.00	42 37	42.22	0 00	40.35	40.53	0.00	44.57	44 96	0.00	
	Greatest difference	1.16	1.60	—	0.92	0.98	—	2.10	1.42	—	1.91	1.38	—	

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TABLE II.—SOLUBLE SOLIDS, PER CENT.

No.	Analyst	Quebracho extract			Hemlock extract			Myrobalans extract			Chestnut oak bark extract			No.
		Slow	Rapid	Difference	Slow	Rapid	Difference	Slow	Rapid	Difference	Slow	Rapid	Difference	
1	Roy H. Wisdom . . .	44.01	44.79	+0.78	39.51	39.33	—0.18	40 11	40.38	+0.27	43.91	44.00	+0.09	1
2	T. S. Dunnigan	43 66	44.08	+0.42	39.33	39.33	0.00	40.13	40 13	0.00	44.00	43.80	—0.20	2
3	W. H. Alsop and J. E. McNutt	44.0	44.8	+0.8	38 75	39.25	+0.50	39.4	39.55	+0.15	43.1	43.3	+0.2	3
4	W. K. Alsop and E. R. Lobaugh . . .	43.9	44.65	+0.65	38.7	38.95	+0.25	39.3	39.5	+0.2	43.3	43.25	—0.05	4
5	C. C. Smoot, III and L. E. Stacy, Jr.	44.28 44.24	45.39 45 39	+1.11 +1.15	38.49 38.25	38.45 38.67	—0.04 +0.22	39.58 39.45	39.70 39.88	+0.12 +0 43	43.53 43.41	43.43 43.53	—0.10 +0.12	5
6	F. P. Veitch, J. S. Rogers and R. W. Frey . . .	44.32	44 54	+0.22	38.56	39.03	+0.47	39.77	40.02	+0.25	43.77	43.61	—0.16	6
7	F. A. Hayes	43.61 43.65	44.61 44.53	+1.00 +0.88	38.71 38.50	38.45 38.27	—0.26 —0.23	37.83[1] 37.81[1]	38.31[1] 38.59[1]	+0.48 +0.78[1]	41.80[1] 41.99[1]	42.35[1] 42.18[1]	+0.55[1] +0.19	7
8	F. O. Sprague and H. J. Newman	44.41	45.29	+0.88	39.16	38.59	—0.57	39.78	40.11	+0.33	43.38	43.55	+0.17	8
9	H. A. Helder	44.27 44.31	44.57 44.57	+0.30 +0.26	39.38 39.41	39.49 39.49	+0.11 +0.08	39.54 39 67	39.89 39.85	+0.35 +0.18	43 56 43 62	43.74 43.79	+0.18 +0.17	9
10	W. A. Fox	43.83	44.16	+0.33	38.61	38 51	—0.10	39.96	39.94	- 0.02	43 72	43.65	—0.07	10
11	H. C. Reed and Geo. W. Toms, Jr. . .	44.12	44.71	+0.59	39.24	39.04	—0.20	39.59	39.85	+0.26	43.41	43.73	+0.32	11
12	C. W. Norris and Adolf Schubert . . .	44.20	44.77	+0.57	39.31	39 08	—0 23	39.69	40.04	+0.35	43.38	43.86	+0.48	12
13	J. M. Seltzer	44.00	44.37	+0.37	38 56	38 64	+0.08	39.74	39.91	+0.17	43.62	43.55	—0.07	13
14	Frank F. Marshall . .	43.57	44.35	+0.78	38 36	38.45	+0.09	39.52	39.67	+0.15	43.55	43 44	—0.11	14

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15	T. S. Greaves	43.77 43.72	44.35 44.96	+0.58 +1.24	39.34 39.46	39.40 39.29	+0.06 —0.17	39.92 39.96	40.04 39.92	+0.12 —0.04	43 70 43.70	43 70 43 55	0.00 —0.15	15
16	C. Rachus	44.47	45.10	+0.63	40.47	40.21	—0.26	40.27	40.39	+0.12	—	—	—	16
17	F. M. Loveland	44.23	44.86	+0.63	39.34	39.22	—0.12	39.84	39.74	—0.10	43.77	43.65	—0.12	17
18	P. M. Randall	45.00	45.25	+0.25	39.21	39.88	+0.67	39.96	41.16[1]	+1.20[1]	44.75[1]	44 55	—0.20	18
19	Thos. A. Faust	44.44 44.64	45.17 45.34	+0.73 +0.70	40.23 39.88	39.89 40.18	—0.34 +0.30	39.98 39.76	40.06 39.89	+0.08 +0.13	43.96 43 86	44.11 —	+0.15 —	19
20	Oskar Riethof	—	—	—	39.25	39.03	—0.22	40.16	40.25	+0.09	43.64	43.55	—0.09	20
21	R. J. Bailey	43.67	44.03	+0.36	38.55	38.31	—0.24	39.90	39.77	—0.13	43.58	42.97	—0.61[1]	21
22	H. L. Pierson	43.87	44.75	+0.88	38.76	38.81	+0.05	39.72	40.03	+0.31	43.48	43.38	—0.10	22
23	Chas. R. Oberfell and F. M. Richeson . . .	43.40	44.17	+0.77	38.83	38.71	—0.12	40.00	39.97	—0.03	43.49	43.75	+0.26	23
24	F. H. Small and V. J. Mlejnek	44.02 44.14	44.96 44.90	+0.94 +0.76	38.88 39.08	38.80 38.88	—0.08 —0.20	39.37 39.45	39.78 39.92	+0.59 +0.47	43.41 43.48	43.35 43.26	—0.06 —0.22	24
25	Thos. J. Mosser	44.14 44 06	44.17 —	+0.03 —	39.39 39.36	39.11 38.96	—0.28 —0.40	38.62 38.84	39.20 39.01	+0.58 +0.17	43.00 43.36	43.35 43.10	+0.35 —0.26	25
26	E. A. Wallin	44.64	45.13	+0.49	38.91	38.72	—0.19	39.95	39.55	—0.40	43.34	43.52	+0.18	26
27	W. S. Loud	44.17	44.49	+0.32	39.65	39.13	—0.52	39.90	39.74	—0.16	43.95	43.99	+0.04	27
28	Theodor Veit	43.58	44.32	+0.74	38.45	38 43	—0.02	39.55	39.34	—0 21	43.70	43.51	—0.19	28
29	R. E. Porter	44.70	44.90	+0.20	38.52	39.05	+0-53	41.20[1]	40.47	—0.73	43.85	44.05	+0.20	29
30	E. R. Olds	44.34	45.45	+1.11	39.98	38.82	—1.16[1]	40.05	40.34	+0.29	44.31	44.30	—0.01	30
	Average	44.08	44.73	+0.65	39.05	39.03	—0.02	39.69	39.84	+0.15	43.57	43.62	+0.05	
	Highest	45.00	45.45	+1.24	39.98	40.21	{+0.63 {—0.57	40.27	40.47	{+0.35 {—0.73	44.31	44.55	{+0.35 {—0.26	
	Lowest	43.40	44.03	+0.03	38.25	38.27	0.00	38.62	39.20	0.00	43.00	42.97	0.00	
	Greatest difference	1.60	1.42	—	1.73	1.94	—	1.65	1.27	—	1.31	1.58	—	

[1] Omitted from average.

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TABLE III.—INSOLUBLES, PER CENT.

No.	Analyst	Quebracho extract			Hemlock extract			Myrobalans extract			Chestnut oak bark extract			No.
		Slow	Rapid	Difference	Slow	Rapid	Difference	Slow	Rapid	Difference	Slow	Rapid	Difference	
1	Roy H. Wisdom	1.51	0.81	−0.70	3.58	3.83	+0.25	1.42	1.13	−0.29	1.73	1.72	−0.01	1
2	T. S. Dunnigan	1.75	1.33	−0.42	3.80	3.87	+0.07	1.35	1.47	+0.12	1.66	1.86	+0.20	2
3	W. K. Alsop and J. E. McNutt	1.65	0.75	−0.9	4.2	3.6	−0.6	2.0	1.9	−0.4	2.3	2.35	+0.05	3
4	W. K. Alsop and E. R. Lobaugh	1.7	1.1	−0.6	4.15	3.8	−0.4	2.3	1.9	−0.4	2.3	2.35	+0.05	4
5	C. C Smoot, III and L. E. Stacy, Jr.	1.22 1.25	0.61 0.35	−0.61 −0.90	4.31 4.58	4.47 4.32	+0.16 −0.26	1.46 1.64	1.72 1.55	+0.26 −0.09	2.17 2.18	2.48 2.26	+0.31 +0.08	5
6	F. P. Veitch, J. S. Rogers and R. W. Frey	1.03	0.78	−0.25	4.26	3.88	−0.38	1.55	1.46	−0.09	1.89	2.04	+0.15	6
7	F. A. Hayes	1.44 1.29	0.53 0.57	−0.91 −0.72	3.82 3.87	3.92 3.95	+0.10 +0.08	2.52 2.54	2.22 2.31	−0.30 −0.23	2.77 2.77	2.61 2.87	−0.16 +0.10	7
8	F. O. Sprague and H. J. Newman	1.57	0.43	−1.14	3.89	3.44	+0.55	1.97	1.50	−0.47	2.14	2.17	+0.03	8
9	H. A. Helder	1.06 0.91	0.57 0.62	−0.49 −0.29	3.16 3.17	3.39 3.39	+0.23 +0.22	2.10 2.00	1.66 1.70	−0.34 −0.30	2.33 2.37	2.13 2.03	−0.20 −0.34	9
10	W. A. Fox	2.17	1.85	−0.32	4.58	4.67	+0.09	1.77	1.76	−0.01	2.37	2.31	−0.06	10
11	H. C. Reed and Geo. W. Toms, Jr. . .	1.25	0.77	−0.48	3.59	3.80	+0.21	1.84	1.59	−0.25	2.53	2.16	−0.37	11
12	C. W. Norris and Adolph Schubert . .	1.27	0.81	−0.46	3.63	3.83	+0.20	1.87	1.62	−0.25	2.53	2.17	−0.36	12
13	J. M. Seltzer	1.65	1.22	−0.43	4.38	4.37	−0.01	1.90	1.68	−0.22	2.09	2.21	+0.12	13
14	Frank F. Marshall . .	1.89	1.22	−0.67	4.50	4.50	0.0	1.77	1.74	−0.03	2.08	2.24	+0.16	14

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15	T. S. Greaves	1.70 1.77	1.13 0.54	—0.57 —0.23	3.64 3.60	3.62 3.85	—0.02 +0.25	1.30 1.41	1.30 1.32	0.00 —0.09	2.04 2.06	2.03 2.23	—0.01 +0.17	15
16	C. Eachus	1.50	0.73	—0.77	2.67	2.95	+0.28	1.48	1.23	—0.25	—	—	—	16
17	F. M. Loveland	1.17	0.58	—0.59	3.51	3.43	—0.08	1.53	1.39	—0.14	1.73	1.79	+0.06	17
18	P. M. Randall	0.81	0 05	—0.76	4.08	2.77	—1.31	1.13	0.56	—0.57	1.60	1.16	—0.44	18
19	Thos. A. Faust	1.51 1.40	0.93 0.60	—0.58 —0.80	2.78 3.19	3.02 2.82	+0.24 —0.37	1.38 1.75	1.28 1.59	—0.10 —0.16	1.70 1.99	1.63 —	—0.07 —	19
20	Oskar Riethof	—	—	—	3.91	4.14	+0.23	1.53	1.51	—0.02	2.40	2.41	+0.01	20
21	R. J. Bailey	1.67	1.60	—0.07	4.34	4.60	+0.26	1.46	1.60	+0.16	2.03	2.73	+0.70	21
22	H. L. Pierson	1.79	0.88	—0.91	4.16	4.33	+0.17	2.04	1.67	—0.37	2.37	2.45	+0.08	22
23	Chas. R. Oberfell and L. M. Richeson	2.10	1.30	—0.80	3.97	4.10	+0.13	1.62	1.67	+0.05	2.31	1.93	—0.38	23
24	F. H. Small and V. J. Mlejnek	1.61 1.38	0.61 0.59	—1.00 —0.79	3.96 3.91	3.94 3.96	—0.02 +0.05	2.16 1.95	1.65 1.49	—0.51 —0.46	2.26 2.23	2.41 2.45	+0.15 +0.22	24
25	Thos. J. Mosser	1.54 1.61	— 1.56	— —0.05	3.37 3.40	3.59 3.87	+0.22 +0.47	2.24 1.88	1.52 1.78	—0.72 —0.10	2.23 2.08	1.82 1.86	—0.41 —0.22	25
26	E. A. Wallin	0.91	0.45	—0.46	4.08	4.09	+0.01	1.55	2.00	+0.45	2.49	2.30	—0.19	26
27	W. S. Loud	1.91	1.34	—0.57	3.51	3.80	+0.29	2.30	2.21	—0.09	2.53	2.35	—0.18	27
28	Theodor Veit	2.11	1.37	—0.74	4.35	4.43	+0.08	1.67	1.84	+0.17	1.99	2.10	+0.11	28
29	R. E. Porter	1.40	1.05	—0.35	4.06	3.81	—0.25	1.25	1.23	—0.02	2.18	1.90	—0.28	29
30	E. R. Olds	1.68	0.72	—0.96	3.12	4.28	+1.16	1.71	1.60	—0.11	1.63	1.82	+0.19	30
	Average	1.51	0.90	—0.61	3.83	3.84	+0.01	1.79	1.62	—0.17	2.21	2.18	—0.03	
	Highest	2.17	1.85	—1.14	4.58	4.60	{+1.16 —1.31	2.54	2.31	{+0.45 —0.72	2.77	2.87	{+0.70 —0.44	
	Lowest	0.81	0.05	—0.05	2.67	2.77	0.0	1.13	0.56	0.0	1.60	1.16	0.0	
	Greatest difference	1.36	1.80	—	1.91	1 83	—	1.41	1.75	—	1.17	1.71	—	

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TABLE IV.—NON-TANNINS.

No.	Analyst	Quebracho extract			Hemlock extract			Myrobalans extract			Chestnut oak bark extract			No.
		Slow	Rapid	Difference	Slow	Rapid	Difference	Slow	Rapid	Difference	Slow	Rapid	Difference	
1	Roy H. Wisdom	10.06	9.98	—0.08	14.30	14.33	+0.03	15.26	15.17	—0.09	19.72	19.81	+0.09	1
2	T. S. Dunnigan . . .	9.86	10.15	+0.29	14.26	14.26	0.0	15.31	15.38	+0.07	19.60	19.25	—0.35	2
3	W. K. Alsop and J. E. McNutt	10.1	9.9	—0.2	13.75	13.75	0.0	15.1	15.05	—0.05	19.4	19.45	+0.05	3
4	W. K. Alsop and E. R. Lobaugh . . .	9.75	9.8	+0.05	13.9	13.9	0.0	15.1	15.15	+0.05	19.4	19.6	+0.2	4
5	C. C. Smoot, III and L. E. Stacy, Jr.	10.14 9.95	10.18 10.05	+0.14 +0.10	14.38 14.65	14.10 14.06	—0.28 —0.59	14.80 14.84	14.71 14.67	—0.09 —0.17	19.74 19.60	19.51 19.40	—0.23 —0.20	5
6	F. P. Veitch, J. S. Rogers and R. W. Frey	10.01	10.00	—0.01	13.96	13.90	—0.06	15.36	15.21	—0.15	20.14	20.00	—0.14	6
7	F. A. Hayes	9.77 9.70	9.96 9.90	+0.19 +0.20	13.31 13.17	13.39 13.31	+0.08 +0.14	14.32[1] 14.16[1]	14.17[1] 14.33[1]	—0.15 +0.17	18.65[1] 18.74[1]	19.01 19.09	+0.36 +0.35	7
8	F. O. Sprague and H. J. Newman . . .	9.71	9.63	—0.08	13.64	13.90	+0.26	15.23	15.14	—0.09	19.36	19.46	+0.10	8
9	H. A. Helder	10.00 9.90	9.79 9.79	—0.21 —0.11	13.82 13.84	13.74 13.74	—0.08 —0.10	15.10 15.10	15.10 15.12	0.0 +0.02	19.62 19.73	19.59 19.52	—0.03 —0.21	9
10	W. A. Fox	9.81	9.87	+0.06	14.19	14.11	—0.08	15.37	15.33	—0.04	19.50	19.57	+0.07	10
11	H. C. Reed and Geo. W. Toms, Jr. . .	10.72	10.75	+0.03	13.97	14.02	+0.05	15.10	15.17	+0.07	19.59	19.60	+0.01	11
12	C. W. Norris and Adolf Schubert . . .	10.76	10.79	+0.03	14.06	14.06	0.0	15.21	15.24	+0.03	19.59	19.65	+0.06	12
13	J. M. Seltzer	9.83	9.82	—0.01	13.87	13.79	—0.08	15.38	15.41	+0.03	19.53	19.71	+0.18	13
14	Frank F. Marshall . .	9.59	9.69	+0.10	13.63	13.65	+0.02	15.01	15.02	+0.01	19.51	19.53	+0.02	14

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15	T. S Greaves	9.99 9.83	9.80 9.86	−0.19 +0.03	14.75 14 35	14.28 14.25	−0 47 −0.10	15.15 14.92	14.93 14.87	−0.22 −0.05	19.32 19.32	19.28 19.25	−0.04 −0.07	15
16	C. Bachaus	10.17	9.97	−0.20	13.75	13.68	−0.07	15.22	15.06	−0.16	—	—	—	16
17	F. M. Loveland	9.34	9.59	+0.25	13.42	13.14	−0.28	15.07	15.01	−0.06	19.26	19.30	+0.04	17
18	P. M. Randall	9.96	9.89	−0.07	13.75	14.48	+0.73	16.08	16.95[1]	+0.87	20.55[1]	20.00	−0.55	18
19	Thos. A. Faust	9.95 10.04	9.76 10.09	−0 19 +0.05	13.80 13.81	13.37 13.60	−0.43 −0.21	15.25 15.19	15.09 15.05	−0.16 −0.14	19.46 19.46	19.27 —	−0.19 —	19
20	Oskar Reithof	—	—	—	13.91	13.68	−0.23	15.37	15.30	−0.07	19.35	19.51	+0.16	20
21	R. J. Bailey	9.72	9.64	−0.08	13.46	13.36	−0.10	15.08	15.19	+0.11	19.40	19.42	+0.02	21
22	H. L. Pierson	12.28[1]	12.30[1]	+0.02	14 39	14.47	+0.08	15.05	15.06	+0.01	19.54	19.62	+0.08	22
23	Chas. R. Oberfell and L. M. Richeson . . .	9.74	9.76	+0.02	13.96	13.96	0.0	15.16	15.15	−0.01	19.52	19.64	+0.12	23
24	F. H. Small and V. J. Mlejnek	9.93 9.86	9.75 9.83	−0.18 −0.03	13.82 13.70	13.73 13.65	−0.09 −0.05	15.07 14.99	15.02 15.02	−0.05 +0.03	19.46 19.50	19.53 19.48	+0.07 −0.02	24
25	Thos J. Mosser	9.91 9.60	9.69 —	−0.22 —	13.60 13 56	13.43 13.48	−0.17 −0.08	15.23 15.25	15.18 15.23	−0.05 −0.02	18.99 19.23	19.13 19 00	+0.14 −0.23	25
26	E. A. Wallin	9.73	9.71	−0.02	13.61	13.55	−0.06	15.11	14.80	−0.31	19.34	19.56	+0.22	26
27	W. T. Loud	10.15	10.05	−0.10	14.61	13.99	−0.62	15.44	15 47	+0.03	19.43	19.22	−0.21	27
28	Theodor Veit	10.02	9.97	−0.05	13.39	13.47	+0.08	15.36	15.32	−0.04	19.67	19.63	−0.04	28
29	R. E. Porter	10.30	10.53	+0.23	13.65	13.77	+0.12	16.61[1]	15.92	−0.69	19.78	19.80	+0.02	29
30	E. R. Olds	10.16	10.16	0.0	14.36	14.15	−0.21	15.23	15.59	+0.36	19.41	19.62	+0.21	30
	Average	9.95	9.93	−0.02	13.90	13.82	−0.08	15.11	15.15	+0.04	19.49	19.48	−0.01	
	Highest	10.72	10.79	{+0.29 −0.22	14.75	14.47	{+0.73 −0.59	16.08	15.92	{+0.87 −0.69	20.14	20.00	{+0.36 −0.55	
	Lowest	9.34	9.59	0.0	13.17	13.14	0.0	14.80	14.67	0.0	18.99	19.01	0.0	
	Greatest difference	1.38	1.20	—	1.58	1.33	—	1.28	1.25	—	1.15	0.99	—	

[1] Omitted from average.

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TABLE V.—TANNINS, PER CENT.

No.	Analyst	Quebracho extract			Hemlock extract			Myrobalans extract			Chestnut oak bark extract			No.
		Slow	Rapid	Difference	Slow	Rapid	Difference	Slow	Rapid	Difference	Slow	Rapid	Difference	
1	Roy H. Wisdon	33.95	34.81	+0.86	25.21	25.00	—0.21	24.85	25.21	+0.36	24.19	24.19	0.00	1
2	T. S. Dunnigan	33.80	33.93	+0.13	25.07	25.07	0.00	24.82	24.75	—0.07	24.40	24.55	+0.15	2
3	W. K. Alsop and J. E. McNutt	33.9	34.9	+1.00	25.0	25.5	+0.5	24.3	24.5	+0.2	23.7	23.85	+0.15	3
4	W. K. Alsop and E. R. Lobaugh . . .	34.15	34.75	+0.60	24.8	25.05	+0.25	24.2	24.35	+0.15	23.9	23.65	—0.25	4
5	C. C. Smoot, III and	34.14	35.21	+1.07	24.15	24.35	+0.20	24.78	24.99	+0.21	23.79	23.92	+0.13	5
	L. E. Stacy, Jr.	34.39	35.34	+0.95	23.60[1]	24.61	+1.01[1]	24.61	25.21	+0.60	23.81	24.13	+0.32	
6	F. P. Veitch, J. S. Rogers and R. W. Frey	34.31	34.54	+0.23	24.60	25.14	+0.54	24.41	24.81	+0.40	23.63	23.61	—0.02	6
7	F. A. Hayes	33.84	34.65	+0.81	25.40	25.06	—0.34	23.51	24.14	+0.63	23.15[1]	23.34[1]	+0.19	7
		33.95	34.63	+0.68	25.33	24.96	—0.37	23.65	24.26	+0.61	23.25[1]	23.09[1]	—0.16	
8	F. O. Sprague and H. J. Newman	34.70	35.66	+0.96	25.52	24.69	—0.83	24.55	24.97	+0.42	24.02	24.09	+0.07	8
9	H. A. Helder	34.27	34.78	+0.51	25.56	25.75	+0.29	24.47	24.79	+0.32	23.94	24.15	+0.21	9
		34.41	34.78	+0.37	25.57	25.75	+0.28	24.57	24.73	+0.16	23.89	24.27	+0.38	
10	W. A. Fox	34.02	34.29	+0.27	24.42	24.40	—0.02	24.59	24.61	+0.02	24.22	24.08	—0.14	10
11	H. C. Reed and Geo. W. Toms, Jr. . .	33.40	33.96	+0.56	25.27	25.02	—0.25	24.49	24.68	+0.19	23.82	24.13	+0.31	11
12	W. C. Norris and Adolf Schubert . . .	33.44	33.98	+0.54	25.25	25.02	—0.23	24.48	24.80	+0.32	23.79	24.21	+0.42	12
13	J. M. Seltzer	34.17	34.55	+0.38	24.69	24.85	+0.16	24.36	24.50	+0.14	24.09	23.84	—0.25	13
14	Frank F. Marshall . .	33.98	34.66	+0.68	24.73	24.80	+0.07	24.51	24.65	+0.14	24.04	23.91	—0.13	14

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15	T. S. Greaves	33.78 33.89	34.55 35.10	+0.77 +0.21	24.59 25.11	25.12 25.04	+0.53 —0.07	24.77 25.02	25.11 25.05	+0.34 +0.03	24.38 24.38	24.42 24.30	+0.04 —0.08	15
16	C. Eachus	34.30	35.13	+0.83	26.72	26.53	—0.19	25.05	25.33	+0.28	—	—	—	16
17	F. M. Loveland	34.89	35.27	+0.38	25.92	26.08	+0.16	24.77	24.73	—0.04	24.51	24.35	—0.16	17
18	P. M. Randall	35.04	35.36	+0.32	25.46	25.40	—0 06	23.88	24.21	+0.33	24.20	24.55	+0.35	18
19	Thos A Faust	34.49 34.60	35.41 35.25	+0.92 +0.65	26.43 26.07	26.52 26.58	+0.09 +0.51	24.73 24.57	24.97 24.84	+0.24 +0.27	24.50 24.40	24.84 —	+0.34 —	19
20	Oskar Riethof	—	—	—	25.34	25.35	+0.01	24.79	24.95	+0.16	24.29	24.04	—0.25	20
21	R. J. Bailey	33.95	34.39	+0.44	25.09	24.95	—0.14	24.82	24.58	—0.24	24.18	24.58	+0.40	21
22	H. L. Pierson	31.59[1]	32.45[1]	+0.86	24.37	24.34	—0.07	24.67	24.97	+0.30	23.94	23.76	—0.18	22
23	Chas R. Oberfell and L. M. Richeson	33.66	34.41	+0.75	24.87	24.75	—0.12	24.84	24.82	—0.02	23.97	24.11	+0.14	23
24	F. H. Small and V. J. Mlejnek	34.09 34.28	35.21 35.07	+1.12 +0.79	25.06 25.38	25.07 25.23	+0.01 —0.15	24.30 24.46	24.76 24.90	+0.46 +0.44	23.95 23.98	23.82 23.78	—0.13 —0.20	24
25	Thos J. Mosser	34.23 34.46	34.48 —	+0.25 —	25.79 25.80	25.68 25.48	—0.11 —0.32	23.39 23.59	24.02 23.78	+0.63 +0.19	24.01 24.13	24.22 24.10	+0.21 —0.03	25
26	E. A. Wallin	34.91	35.42	+0.51	25.30	25.17	—0.13	24.84	24.75	—0 09	24.00	23 96	—0.04	26
27	W. S. Loud	34.02	34.44	+0.42	25.05	25.14	+0.09	24.46	24.27	—0 19	24.52	24.77	+0 25	27
28	Theodor Veit	33.56	34.35	+0.79	25.06	24.96	—0.10	24.19	24.02	—0.17	24.03	23.88	—0.15	28
29	R. E. Porter	34.40	34.37	—0.03[1]	24.87	25.28	+0.41	24.59	24.55	—0.04	24.07	24.25	+0.18	29
30	E. R. Olds	34.18	35.29	+1.11	25.62	24.67	—0.95	24.82	24.73	—0.09	24.90	24.68	—0.22	30
	Average	34.15	34.78	+0.63	25.21	25.21	0.00	24.46	24.65	+0.20	24.06	24.08	+0.02	
	Highest	35.04	35.66	+1.12	26 72	26.58	{+0.54 —0.95	25.06	25.33	{+0.63 —0.24	24.90	24.84	{+0.42 —0.30	
	Lowest	33.40	33.93	+0.13	24.15	24.35	0.00	23.39	23.78	{+0.02 —0.02	23.63	23.09	0.00	
	Greatest difference	1.64	1.73	—	2.57	2.23	—	1.67	1.55	—	1.27	1.75	—	

[1] Omitted from average.

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TABLE VI.—TANNINS, SHOWING DEVIATION FROM THE MEAN.

No.	Analyst	Quebracho extract				Hemlock extract				Myrobalans extract				Chestnut oak bark extract				No.
		Slow	Deviation	Rapid	Deviation	Slow	Deviation	Rapid	Deviation	Slow	Deviation	Rapid	Deviation	Slow	Deviation	Rapid	Deviation	
1	Roy H. Wisdom . . .	33.95	—0.20	34.81	+0.03	25.21	0.00	25.00	—0.21	24.85	+0.39	25.21	+0.55	24.19	+0.13	24.19	+0.11	1
2	T. S. Dunnigan . . .	33.80	—0.35	33.93	—0.85	25.07	—0.14	25.07	—0.14	24.82	+0.36	24.75	+0.09	24.40	+0.34	24.55	+0.47	2
3	W. K. Alsop and J. E. McNutt	33 9	—0.25	34.9	+0.12	25.0	—0.21	25.5	+0.29	24.3	—0.16	24.4	—0.16	23.7	—0.36	23.85	—0.23	3
4	W. K. Alsop and E. R. Lobaugh	34 15	0.0	34.75	—0.03	24.8	—0.41	25.05	—0.16	24.2	—0.26	24.35	—0.28	23 9	—0.16	23.65	—0.43	4
5	C. C. Smoot, III and L. E. Stacy, Jr.	34.14 34.39	—0.01 +0.24	35.21 35.34	+0.43 +0.56	24.15 23.60[1]	—1.06 —	24.35 24.61	—0.86 —0.60	24.78 24.61	+0.32 +0.15	24.99 25.21	+0.33 —0.45	23.79 23.81	—0.27 —0.25	23.92 24.13	—0.16 +0.05	5
6	F. P. Veitch, J. S. Rogers and R. W. Frey	34.31	+0.16	34.54	—0.24	24.60	—0.61	25.14	—0.07	24.41	—0.05	24.81	+0.15	23.63	—0.43	23.61	—0.47	6
7	F. A. Hayes	33.84 33.95	—0.31 —0.20	34.65 34.63	—0.13 —0.15	25.40 25.33	+0.19 +0.12	25.06 24.96	—0.15 —0.25	23.51 23.65	—0.95 —0.81	24.14 24.26	—0.52 —0.40	23.15[1] 23.25[1]	— —	23.34 23.09	—0.74 —0.99	7
8	F. O. Sprague and H. J. Newman . .	34.70	+0.55	35.66	+0.88	25.52	+0.31	24.69	—0.52	24.55	+0.09	24.97	+0.31	24.02	—0.04	24.09	+0.01	8
9	H. A. Helder	34.27 34.41	+0.12 +0.26	34.78 34.78	0.00 0.00	25.56 25.57	+0.35 +0.36	25.75 25.75	+0.54 +0.54	24.47 24.57	+0.01 +0.11	24.79 24.73	+0.13 +0.07	23.94 23.89	—0.12 —0.17	24.15 24.27	+0.07 +0.19	9
10	W. A. Fox	34.02	—0.43	34.29	—0.49	24.42	—0.79	24.40	—0.81	24 59	+0.13	24.61	—0.05	24.22	+0.16	24.08	0.00	10
11	H. C. Reed and Geo. W. Toms, Jr. .	33.40	—0.75	33.96	—0.82	25.27	+0.06	25.02	—0.19	24.49	+0.03	24.68	+0.02	23.82	—0.24	24.13	+0.05	11
12	C. W. Norris and Adolf Schubert . .	33.44	—0.71	33.98	—0.80	25.25	+0.04	25.02	—0.19	24.48	+0.02	24.80	+0.14	23.79	—0.27	24.21	+0.13	12
13	J. M. Seltzer	34.17	+0 02	34 55	—0.23	24.69	—0.52	24.85	—0.36	24.36	—0.10	24.50	—0.16	24.09	+0.03	23.84	—0.24	13
14	Frank F. Marshall .	33.98	—0.17	34.66	—0.12	24.73	—0.48	24.80	—0.41	24.51	+0.05	24 65	—0.01	24.04	—0.02	23.91	—0.17	14

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15	T. S. Greaves	33.78 33.89	−0.37 −0.26	34.55 35.10	−0.23 +0.32	24.59 25.11	−0.62 −0.10	25.12 25.04	−0.09 −0.17	24.77 25.02	+0.31 +0.56	25.11 25.05	+0.45 +0.39	24.38 24.38	+0.32 +0.32	24.42 24.30	+0.34 +0.22	15
16	C. Eachus	34.30	+0.15	35.13	+0.35	26.72	+1.51	26.53	+1.32	25.05	+0.59	25.33	+0.67	—	—	—	—	16
17	F. M. Loveland . . .	34.89	+0.74	35.27	+0.49	25.92	+0.71	26.08	+0.87	24.77	+0.31	24.73	+0.07	24.51	+0.45	24.35	+0.27	17
18	P. M. Randall	35.04	−0.11	35.36	+0.58	25.46	+0.25	25.40	+0.19	23.88	−0.58	24.21	−0.45	24.20	+0.14	24.55	+0.47	18
19	Thos. A. Faust	34.49 34.60	+0.34 +0.45	35.41 35.25	+0.63 +0.47	26.43 26.07	+1.22 +0.86	26.52 26.58	+1.31 +1.37	24.73 24.57	+0.27 +0.11	24.97 24.84	−0.31 +0.18	24.50 24.40	+0.44 +0.34	24.84 —	+0.76 —	19
20	Oskar Riethof	—	—	—	—	25.34	+0.13	25.35	+0.14	24.79	+0.33	24.95	+0.29	24.29	+0.23	24.04	−0.04	20
21	R. J. Bailey	33.95	−0.20	34.39	−0.39	25.09	−0.12	24.95	−0.26	24.82	+0.36	24.58	−0.08	24.18	+0.12	24.58	+0.50	21
22	H. L. Pierson	31.59[1]	—	32.45[1]	—	24.37	−0.84	24.34	−0.87	24.67	+0.21	24.97	+0.31	23.94	−0.12	23.76	−0.32	22
23	Chas. R. Oberfell and L. M. Richeson . .	33.66	−0.49	34.41	−0.37	24.87	−0.34	24.75	−0.46	24.84	+0.38	24.82	+0.16	23.97	−0.09	24.11	+0.03	23
24	F. H. Small and V. J. Mlejnek	34.09 34.28	−0.06 +0.13	35.21 35.07	+0.43 +0.29	25.06 25.38	−0.15 +0.17	25.07 25.23	−0.14 +0.02	24.30 24.46	−0.16 0.00	24.76 24.90	+0.10 +0.24	23.95 23.98	−0.11 −0.08	23.82 23.78	−0.26 −0.30	24
25	Thos. J. Mosser . . .	34.23 34.46	+0.08 +0.31	34.48 —	−0.30 —	25.79 25.80	+0.58 +0.59	25.68 25.48	+0.47 +0.27	23.39 23.59	−1.07 −0.87	24.02 23.78	−0.64 −0.88	24.01 24.13	−0.05 +0.07	24.22 24.10	+0.14 +0.02	25
26	F. A. Wallin	34.91	+0.76	35.42	−0.36	25.30	+0.09	25.17	−0.04	24.84	+0.38	24.75	+0.09	24.00	−0.06	23.96	−0.12	26
27	W. S. Loud	34.02	−0.13	34.44	−0.34	25.05	−0.16	25.14	−0.07	24.46	0.00	24.27	−0.39	24.52	+0.46	24.77	+0.69	27
28	Thedor Veit	33.56	−0.59	34.35	−0.43	25.06	−0.15	24.96	−0.25	24.19	−0.27	24.02	−0.64	24.03	−0.03	23.88	−0.20	28
29	L. E. Porter	34.40	+0.25	34.37	−0.41	24.87	−0.34	25.28	+0.07	24.59	+0.13	24.55	−0.11	24.07	+0.01	24.25	+0.17	29
30	F. R. Olds	34.18	+0.03	35.29	+0.51	25.62	+0.41	24.67	+0.54	24.82	+0.36	24.73	+0.07	24.90	+0.84	24.68	+0.60	30
		Average	Average deviation	Average	Average deviation	Average	Average deviation	Average	Average deviation	Average	Average deviation	Average	Average deviation	Average	Average deviation	Average	Average deviation	
		34.15	0.275	34.78	0.36	25.21	0.42	25.21	0.40	24.46	0.30	24.66	0.27	24.06	0.22	24.08	0.28	

[1] Omitted from average and deviation.

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CHAS. C. SMOOT, III.: While the results as a whole are very close, the greater uniformity is found in the slowly cooled solution. The value of this work done in this way, to my mind, is doubtful, because of the fact that the non-tannins were determined in both solutions with hide chromed by the slow method, while in actual practice, if the analyst desired to gain time by rapid cooling, he would, of course, use rapidly chromed hide to detannize his solutions. Therefore, I can see no real value in a comparison such as we have made.

F. P. VEITCH: The only comment that I can make on these results, is that possibly the difference between the two methods for cooling would have been greater on the quebracho extract had this sample contained a high percentage of insolubles.

F. A. HAYES: The quebracho shows markedly less insolubles and greater tan by the quick cooling. Work on quebracho containing higher and lower per cent. insolubles should be done before any final conclusions are made. Myrobalans show a similar but less marked condition.

H. A. HELDER: I followed the A. L. C. A.'s methods as closely as possible and found no extreme variations in the two methods of cooling used; however, I am partial to the old method of slow cooling.

W. A. FOX: From my results as well as previous experience accurate and concordant results can be obtained by either method of cooling. Clear filtrates, the essential thing, are hard to get in some few cases, but do not necessarily depend on the rate of cooling.

H. C. REED AND C. W. NORRIS: The quebracho extract gives a solution difficult to filter clear; more difficult in the case of the slow than with the rapid cooled solution. The hemlock gives more brilliant soluble solids solutions with the rapid than with the slow cooling. The myrobalans a more brilliant soluble solids filtrate from the slow than from the rapid cooling. All the filtrates taken in themselves might be considered "clear," but there are degrees of clarity shown by comparisons of one filtrate with another. We have in the case of the quebracho extract an example of a clarified extract that gives quite different results by the rapid and slow cooling methods, a difference as shown by

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our results amounting to nearly ½ per cent. in insolubles and in tannin, as there appears to be no difference in the non-tannin figures. The same may be said of the chestnut oak bark extract, although we are not entirely confident that this will always hold true with other makes of this extract. But in the case of the quebracho extract numerous tests have convinced us that this particular make of extract will always give results showing approximately the differences between the rapid and slow cooling methods that we here obtain. The hemlock extract differs from the quebracho, oak and myrobalan extracts in giving higher insolubles by the rapid than by the slow cooling method. The myrobalan extract shows approximately ¼ per cent. more tannin by the rapid than by the slow cooling method. The temperatures of solutions standing over night were in every instance 20° C. in the morning, and the room temperatures were at 20° C. throughout filtrations. The result of our work seems to indicate that tannin solutions containing any appreciable amount of insolubles will give different results by the two methods with practically no difference in non-tannins, thus making a difference in the tannin figure corresponding to the difference in the item of soluble solids. We are forced to the conclusion that some steps must be taken to alter the official method in recognition of the discrepancies shown.

J. M. SELTZER: All results are the averages of closely agreeing duplicates, and "Official Method of the American Leather Chemists Association" 1915 were followed throughout in all details. *Oak Bark Extract.*—This extract gave a tannin percentage of 0.25 per cent. lower by rapid cooling method caused by higher insolubles and also by higher non-tannins. The soluble solids were clear by transmitted light, slightly opalescent by reflected light, non-tannins were slightly opalescent. *Hemlock Extract.*—The tannin by the rapid cooling method was 0.16 per cent. higher than by slow cooling and was caused by non-tannins being slightly lower. Both methods gave some insolubles. Solubles solids were clear and non-tannins slightly opalescent. *Myrobalan Extract.*—The tannin was 0.14 per cent. higher by rapid cooling method caused by lower insolubles. Soluble solids and non-tannins were clear in both cases. *Quebracho Extract.*—

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The tannin by the rapid cooling method was 0.38 per cent. higher caused by lower insolubles. The difference in appearance of the total solids solutions by slow and rapid cooling was very marked, the former was quite cloudy and opaque, the latter showed much less insoluble matter and was transparent. It has often been shown that the rapid cooling method does not give concordant results when compared with the slow cooling method. The writer thinks that the rapid cooling provision should be removed from the method of the A. L. C. A. as it seems to be there merely for the sake of an occasional analysis, and since by far the greater percentage of analysis are made by the slow cooling method, it is the writer's thought that the method should be so specific and not contain an alternative method.

FRANK F. MARSHALL: In all cases I find that the rapid cooling gave higher total and soluble solids. The non-tannins and tannins were quite constant with the exception of the quebracho extract, where the rapid cooling did not precipitate as much insoluble matter, thereby causing a higher tannin percentage. The soluble solids were all clear, excepting the quebracho, which showed a slight opalescence by reflected light. The non-tannins of the oak and hemlock extracts also showed a slight opalescence. The official method was used throughout these analyses.

GEO. A. KERR AND T. S. GREAVES: No. 1 F. 15 cm. diameter Swedish filter paper was used throughout, discarding those which showed pin holes when held up to the light. In the case of the slow cooling the temperature at which they stood over night is indicated. They were then brought the rest of the way to 20° C. by a little rapid cooling. They were kept above 20° to insure their not going below that temperature. In no case was any difference in rate of filtration noticed between the two methods. *Hemlock Extract.*—Slow cooled were kept overnight at 28° C. Slow cooled non-tannin solutions were redder before filtering than the rapid cooled. After filtering both were alike, pale. Hide powder used showed in degree of redness the converse of non-tannin solution. *Chestnut Oak Bark Extract.*—Slow cooled kept over night at 24° C. Before filtering non-tannin solutions of slow cooled were darker, and of the rapid cooled, lighter; hide powders showed the reverse, and the difference in the non-tannin

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solutions disappearing when filtered, as with hemlock. *Quebracho Extract.*—Over night at 24° C. non-tannin solutions alike for all four analyses. The analytical solutions of this extract during the analysis showed a distinct difference between the slow and rapid cooled, the slow cooled being opaque and the rapid cooled clear. After twenty-four hours this difference was about the same. After a week the clear, rapid cooled solutions had become so opaque that they could barely be dstinguished from the slow cooled. During the time contact and afterwards the filter papers of the rapid cooled were decidedly more yellow than those of the slow cooled, which was the color that would have been expected from the extract color. After filtering the rapid cooled soluble solid solution had a yellowish tinge as compared with the slow cooled. *Myrobalans.*—No difference was noticed here between slow and rapid cooled. Kept overnight at 24½° C. We suggest that the difference in non-tannin solution colors in oak bark and hemlock, due to the rapid cooling, throwing down the insolubles faster, causes them to agglutinate and thus be mechanically removed more completely by the hide powder. This agrees with all the facts observed and seems to be the best explanation obtainable. Also think that the yellow color of the filter paper of the rapid cooled quebracho may have considerable significance in view of the dyeing properties of this extract. The peculiarities of the quebracho rapid cooling analyses and the solution appearance we have not explained, not having sufficient evidence. We note that ordinary quebracho was suggested by the council and that treated extract was sent out, so will append results on a sample of dry quebracho which we have here, one that we suppose to be untreated.

APPENDED RESULTS ON UNTREATED QUEBRACHO.

	Slow cooled		Rapid cooled	
	I	II	I	II
Total solids	90.82	91.03	91.01	91.74
Soluble solids	82.03	81.82	83.00	82.67
Insolubles	8.79	9.21	8.01	8.87
Non-tannin	7.64	7.31	7.22	7.26
Tannin	74.39	74.51	75.78	75.61

The solutions for these four analyses were made by emptying the contents of the weighing bottle into the beaker, running in

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about 200 cc. of hot water and stirring until dissolved, then pouring into the flask and completing in usual manner. Kept over night at 24° C. In this case the characteristic color of the filter paper for the two methods was the same as for treated quebracho. A difference in opacity was not noticed because of the large amount of insoluble material, but a corresponding difference in color of the unfiltered analytical solutions was observed, the rapid cooled being considerably lighter. The analyses of the untreated show peculiarities similar to those of the treated.

FRANK M. LOVELAND: The slow cooled extracts were made up according to the official method and allowed to come to room temperature by standing over night, and brought to 20° C. the following morning. The rapid cooled were made up in the morning and brought quickly to 20° C. by constant agitation in a water jacket with a temperature of not less than 19° C. The same lot of hide-powder was used for both sets of extracts and was allowed to chrome over night by the slow method. We used S. & S. No. 590, 15 cm. diameter filter paper for our non-tannins. The hemlock and oak bark extracts filtered very slowly, it taking almost three hours to collect our soluble solids filtrates for these two extracts. We noted no difference in the appearance of the filtrates on these two extracts by the slow or rapid cooled method, and the analyses seem to bear this out. As regards the myrobalan extract, this settled out very badly before we were ready to analyze it and it was difficult to get the insolubles back into an intimate mixture. On filtering this extract the rapid cooled extract came through slightly faster than the slow cooled and it did not appear quite as brilliant. The quebracho extract that had been slow cooled, gave a much more brilliant soluble solid filtrate than the rapid cooled and the increase in insolubles bears out this fact. From the results on these four extracts it would seem that the oak, hemlock and myrobalans gave very close results and that either method could be used with satisfactory results. With the quebracho this does not bear out, as the rapid cooled extract gives the lower precentage of insolubles. However, in our opinion these two methods should not be interchangeable. We have done considerable work on extracts over the period since these two methods have been official and while concordant results may

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be obtained on some extracts, yet others made from the same material will show insolubles entirely at variance. The rapid cooling method no doubt enables a chemist to turn out results in a shorter time on a few samples of extract, but a concordance of results between laboratories is more highly desirable and it is our opinion that the slow cooling method is far more apt to lead to this desired end.

THOS. A. FAUST: The principal point to be noted from these results is the much better concordance both in insolubles and in tannin, secured by the rapid cooling method than by the slow cooling method. This variation in insolubles is great, depending entirely on the temperature of the solutions during the night while they are cooling. Furthermore, extracts analyzed in the summer will give considerably lower insolubles than extracts analyzed in the winter time, even though the solutions do not at any time cool below 20°. It appears that on high insoluble extracts the variations by the slow cooling method are considerable, whereas the variations by the rapid cooling method are much less. In the case of quebracho extracts, the insolubles by the rapid cooling method are generally much lower than by the slow cooling method, but on hemlocks, myrobalans and oaks I have never noticed any concordant difference either way. I have always favored the slow cooling method but the work which I have done during the past year, and this committee work which I have carried out, leads me to believe that the rapid cooling method is more accurate. Furthermore, recent conditions in the trade are such that it is necessary for the association to adopt one or the other of the two methods. It is a well-known fact that manufacturers of extract are to-day selling extract on the rapid cooling method, and tanners are purchasing it on the slow cooling method, with the natural consequences. My conclusion, therefore, is that it is necessary for us to eliminate the slow cooling method.

OSKAR RIETHOF: In 44 tests on hemlock extract, both slow and rapid cooling, showed in 35 cases higher insolubles on rapid cooling, the average being 0.34 per cent. In 39 cases the non-tannins were lower on rapid cooling, the average being 0.16 per cent. The percentage of tannin, therefore, was 0.18 per cent. lower by rapid cooling. There is no doubt but that rapid cooling

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gives lower results on hemlock extract. For a time I was handicapped on account of lack of filter paper No. 590 and I couldn't get reliable results with Swedish 1 F.

H. L. PIERSON: I would add that the hemlock filtered brilliant in each case, immediately. The oak gave a brilliant filtrate by the over night method immediately; filtered clear after discarding about 50 cc. by the quick method. The myrobalans yielded clear filtrates in both methods, immediately by the quick method and after discarding 100 cc. in the slow method. Neither method gave brilliant filtrates. I would add that the oven gave trouble during the night of heating the hemlock and oak, consequently the required time of heating was not exact.

THOS. J. MOSSER: It seems to me that one or the other of the two methods of cooling the extract solutions should be abandoned as I find that by the rapidly cooling method I generally get slightly lower insolubles and I also find that it is very difficult to get absolutely clear filtrates with the rapidly cooled solutions. This is the one that should be abandoned for the only advantage to be gained by it is the matter of time, which is only a matter of a few hours in arriving at results.

W. S. LOUD: It seems to me that it might be well to try a test wherein the cooling water would be maintained at a point 10° to 15° under that of the extract solutions being cooled. From tests I have made the results seem to approach nearer those given by the slow method. Solutions were cooled to 20° C. in 45 minutes, cooling water being maintained at 20° C. plus contents of flasks being agitated every 3 or 4 minutes. Analyses were carried out at 23°.

DR. VEIT: In former experiments I had found that the temperature of the contents of the liter flask immediately after the transfer of the solution made with water at 85° C. is only 73°-78° C. For this reason I added a third set of tests in which the solution in the flask was brought up to 85° C. again before cooling (C). Furthermore, for the sake of comparison, I took in another set of tests in which the dissolving and cooling were carried out according to the directions of the International method (D). C. Dissolved with water at 85° C. rapid cooled,

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but heated in 1 liter flask to 85° before cooling. D. Dissolved with boiling water, rapid cooling (international method).

	Quebracho		Myrobalans		Chestnut oak		Hemlock	
	C	D	C	D	C	D	C	D
Tannin	34.72	34.75	24.32	24.42	24.04	23.83	25.26	25.26
Non-tans	9.82	9.77	15.11	15.11	19.60	19.71	13.32	13.25
Insolubles	0.98	1.04	1.72	1.64	1.97	2.22	4.33	4.37
Water	54.48	54.44	58.85	58.83	54.39	54.24	57.09	57.12
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

R. E. PORTER: The only consistent difference between the slow cooling and rapid cooling that I can notice in my work is the higher per cent. of insolubles in the slow cooling.

E. A. WALLIN: *Quebracho.*—In the rapidly cooled solution the total solids solution was clearer than the slowly cooled. It also showed higher tannin, due to less insolubles. *Hemlock.*—Very little difference was noticed between two methods, except that the slow cooled sample showed a little higher tannin. *Oak Bark.*—No appreciable difference noticed.

EDWIN R. OLDS: By the following results it seems to me that the slow method is the more reliable one of the two methods, because when analyzing a quebracho extract you are getting results which benefits the buyer whereby the rapid method benefits the seller, but in analyzing a hemlock extract my above statement would be vice versa, that is the slow method would benefit the seller whereby the rapid method would benefit the buyer. In analyzing myrobalan or oak I believe either method can be used, given the analyst results which can be relied upon. Therefore, I believe the method used in analyzing any extract should be mentioned on all reports. I wish to make a slight comment upon the reports I have sent you, referring to the high results, which I made on the total solids, soluble solids and non-tannins. This error is caused by the evaporator, but, at the same time, I believe it brings out the point, that the method used (rapid or slow cooling) should be mentioned on all extract reports.

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REPORT OF COMMITTEE ON HARD GREASES.

By T. A. Faust.

The Committee for the year 1914 did some preliminary work on this subject, report of which was given at the last Convention and published in the December number of the JOURNAL.

The methods considered were melting point, both on fats and paraffine wax; free oil in paraffine wax; unsaponifiables; titer test and acid value.

It was thought that with the exception of the melting point of paraffine wax, no laboratory work was necessary, and that the work of the Committee lay principally in standardizing existent reliable methods for the various determinations, and the selection of a method for ascertaining the amount of free oil in paraffine wax. The latter problem was abandoned, as it was found that while various methods would give fairly good results, the importance of the determination was not worth the amount of trouble necessary to secure a method.

The collaborative work carried out on the melting point of paraffine wax indicated that either the English or Saybolt method gives reliable results in the hands of various operators, and that there is no considerable difference in the results between the two methods.

It was suggested, however, that some laboratory work be carried out by this year's committee on the methods for determining the melting point of fats; consequently the chairman sent out a sample of oleo stearine and a sample of recovered grease, together with the following directions to be pursued in determining which method would give the better results.

Melting Point.—(All greases except paraffine wax.)

Method A: Draw the melted fat up into a small glass capillary tube (about 2 mm. in diameter) to a distance of about 10 mm., and allow to cool over night. Fasten the tube to a thermometer with an elastic band, so that the grease is level with the mercury bulb, and suspend in a beaker of water which is heated slowly. The temperature at which the grease becomes clear and rises in the tube is called the melting point.

Method B: Dip a thermometer into the melted grease so that

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a film of grease covers the entire bulb. After standing over night, place the thermometer in a test-tube, lightly corked, so that the bulb is 1 in. from the bottom of the tube. Suspend the test-tube over asbestos gauze, the bottom of the tube being 1 in. above the gauze. Place a flame beneath, and gradually raise the temperature until a drop of clear grease forms on the bottom of the bulb; this temperature represents the melting point.

The accompanying table shows the results obtained by the various collaborators, on both samples, by Methods A and B. There seems to be considerable variation, there being a maximum difference in the case of oleo stearine of 5½° by Method A, and 4½° by Method B; in the case of recovered grease, the difference was about 8 °by Method A, and excluding one result, about 5° by Method B. However, on averaging the results, excluding a few which were abnormal, the difference between the average and the extreme is, in the case of oleo stearine, about 3°, and in the case of the recovered grease, about 4°; but Method B gave much more concordant results than Method A. Several suggestions were offered by the various members of the Committee, as follows:

Mr. Orthmann is in favor of the Ubbelohde apparatus.

Mr. Alsop objects to Method A, *i. e.*, using a tube open at each end; and made determinations by various slight alterations of Method A, which showed considerable variation. (See table.)

Mr. Oberfell suggests that in view of objections common to all methods, the one giving the most concordant results by the various members of the Committee should be preferred.

Mr. Small objects to the size of the capillary tube, stating that it should be not over 1 mm. in diameter, and should be sealed at the lower end after the introduction of the grease; also that the temperature at which the grease becomes transparent should be taken as the melting point.

Regarding Method B, he suggests that the test-tube, containing the thermometer and grease, should be immersed in a beaker of water, rather than suspended over asbestos gauze, insuring a more uniform rise of temperature.

Mr. Esten carried out some work to determine variations due to a varying time of raise of temperature, and found that rapid

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heating tends to give high results by Method A, and low results by Method B. He suggests that the temperature be raised not more than 1½° per minute.

Conclusions: In view of the fact that the results reported indicate that there is some difficulty in getting agreement between various operators, the chairman thought it advisable to leave the matter of melting point of fats (other than paraffine wax) open until the coming Convention, and have the matter discussed fully at that time.

OLEO STEARINE.

	Method A Degrees			Method A Degrees	
Esten	122¼			122¼	117½ [1]
Small & Vaudreuil	122	125¾ [2]		124¾	126¼ [3]
Sprague	125½			136½	
	123¾				
Orthmann	127½			125½	
	127½			126½	
Alsop & Cuthbert	123¾	124	121	122¾	
	124½	124½ [4]	121 [5]	123¼	
		124¾	121		
Eachus	123			124	
Oberfell	124			122	
	123			122	
Faust & Kernahan	126			122	

RECOVERED GREASE.

Esten	101¾			102¼	
Small & Vaudreuil	102¾	108½ [2]		107	108¼ [3]
Sprague	105¾			107½	
	107½				
Orthmann	109½			112	
	109½			112½	
Alsop & Cuthbert	106¼	105	101¼	104¼	
	106¾	106¾ [4]	101¼ [5]	105	
	107¼	108¾	101¼		
Eachus	105			106	
Oberfell	104			107	
	103			106	
Faust & Kernahan	108			106	

[1] Temperature raised quickly—2.3° per minute.
[2] Capillary tube sealed at lower end.
[3] Test-tube immersed in beaker of water.
[4] Air bubbles in tube above grease.
[5] Tube only partially submerged in water.

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It appears that Method B, with certain alterations, such as immersing the test-tube and thermometer in a beaker of water, as per Mr. Small's suggestion, thus insuring a more uniform distribution of the heat; and limiting the rise of temperature per minute, would give very good results.

No collaborative work was done on any other determinations, but the chairman submitted to the Committee the following rewritten directions for determination of melting point of paraffine wax; unsaponifiables; titer test and free fatty acids.

Melting Point of Paraffine Wax.—Fill a test-tube (about 1 in. in diameter) with the melted paraffine wax to a depth of about 2 in. Insert a small thermometer and stir the mass steadily while the test-tube and its contents are allowed to cool slowly. The temperature at which the thermometer remains stationary for about ½ minute is the melting point.

Titer Test.—Former provisional method, excluding description of standard thermometer.

Unsaponifiables.—The method suggested for unsaponifiables in moellons, as follows: Weigh accurately in a 300 cc. flask, 5 grams of the grease, add 2.5 grams caustic potash dissolved in a little water (or 5 cc. of a 50 per cent. KOH solution) and 25 cc. of 95 per cent. alcohol, boil with reflux condenser for 1 hour, shaking occasionally. Glass beads may be used to prevent bumping. Add 50 cc. hot water, cool, transfer to a separatory funnel, and extract three times, using 40 cc. petroleum ether for each extraction. A little alcohol may be added to break persistent emulsions. Wash the combined ether solution three times with a mixture of 30 cc. of water and 10 cc. of alcohol, transfer to a tared dish, evaporate to dryness, cool and weigh. Excessive drying must be avoided.

Free Fatty Acids.—The method suggested for free fatty acids in moellons, as follows: Weigh out 1 gram grease, dissolve in mixture of 20 cc. alcohol and 20 cc. sulphuric ether, which has been neutralized to phenolphthalein, and titrate with N/10 NaOH, using phenolphthalein as indicator. Test for mineral acids or alkalies (by adding methyl orange to the water emulsion of the moellon), and if present, make the necessary correction.

Comments: The methods for melting point of paraffine wax,

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titer test, unsaponifiable and free fatty acids, were considered satisfactory by the various members of the Committee.

Mr. Eachus, however, brought up the point that the method as proposed for moellons will not work with greases melting over 120° F., in that the saponification will not be complete, and that the best way is to use some petroleum ether with the potash and alcohol.

ANALYSIS OF LACTIC ACID.

Report of 1915 Committee.

By L. Balderston, Chairman.

Volatile Acid.

Test of C. P. Sample.—Following out the line suggested in last year's report, the Chairman made a series of experiments on the determination of volatile acid in lactic acid by distillation. First, McLauchlan's results[1] were confirmed, in regard to the carrying over of lactic acid by steam. A sample of C. P. concentrated lactic acid was diluted so as to contain about 3 per cent. acid. Of this solution, 150 cc. were placed in a round-bottomed Kjeldahl flask with long neck, connected through a Kjeldahl bulb to a spiral condenser, and 125 cc. were distilled over in about 50 minutes. To the residue, 125 cc. of water were added, and again 125 cc. distilled over. The first distillate neutralized from 0.7 to 0.9 cc. of N/10 NaOH, the average of six being 0.8 cc. The second distillate required from 0.6 to 0.8, average of six, 0.7 cc. The fact that the second distillate contains nearly as much acid as the first makes it very improbable that we have here to do with volatile acid. The neutralized distillates were evaporated down to small volume, filtered to remove phenolphthalein, and finally evaporated to dryness at 95° C. The residue, if it were sodium acetate, would contain 54 milligrams of acetic acid, quite enough to give a qualitative test. On comparing it with a corresponding quantity of sodium acetate, both being treated with alcohol and sulphuric acid, it was evident that the residue was not an acetate. The sample of lactic acid used was therefore assumed to contain no volatile acid.

[1] Journal, vol. II, p. 15.

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Effect of Height of Distilling Apparatus.—Some of the same dilution used in the above experiments was distilled in an apparatus similar to that described except that the flask had a short neck and the total height was 8 inches instead of 20. In this case 125 cc. distilled over from 150 required 3.4 cc. of 0.1 N NaOH, quite four times as much as in the case of the tall apparatus.

Rate of Distillation.—A mixture of lactic and acetic acids was made up, and 125 cc. distilled over from 150 at varying rates. The times and the quantities of 0.1 N NaOH required to neutralize the distillate were as follows: 28 minutes, 21 cc.; 31 minutes, 20.1 cc.; 38 minutes, 19 cc.; 66 minutes, 18.4 cc.; 67 minutes, 18.1 cc.; 71 minutes, 17.2 cc. A second set of six with another solution gave the following: 30 minutes, 20 cc.; 32 minutes, 20.3 cc.; 38 minutes, 19.8 cc.; 40 minutes, 19.6 cc.; 43 minutes, 18.2 cc.; 92 minutes, 16.4 cc. Another set of six was run with a solution of the same C. P. lactic acid used in the experiment first described. Four of these were with standard apparatus, with these results: 33 minutes, 1.4 cc.; 35 minutes, 1.4 cc.; 68 minutes, 0.6 cc.; 68 minutes, 0.7 cc. Two used the short apparatus and gave the following: 20 minutes, 2.9 cc.; 108 minutes, 1.7 cc. It is very evident that more rapid boiling causes more acid to be carried over, other things being the same.

Catching Distillate Under Water.—In all the experiments so far described, the distillate was allowed to drop into the receiver. In order to test whether this causes any loss, a set of six was run, four with standard apparatus and two with delivery tubes ending under water in the receivers. The first four gave the following results, 125 cc. being distilled from 150 in about 50 minutes: 10.7 cc., 10.8 cc., 10.8 cc., and 10.7 cc. 0.1 N NaOH respectively to neutralize the distillates. One of those whose distillate was caught under water took the same time, and 125 cc. were distilled over. It took 10.7 cc. 0.1 N NaOH. The other was a few minutes less in time, and by mistake 3 cc. too much was distilled over, it being hard to control the amount closely because of the disturbance in the receiver due to the entrance of the steam. The number of cubic centimeters of soda in this case was 11.2. It was decided that no appreciable loss occurs.

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Behavior of Propionic Acid.—A sample of C. P. propionic acid was tested by diluting 2 grams to 250 cc. and titrating 25 cc. portions with a tested 0.1 N NaOH solution. The acid figured out 101.3 per cent pure. Assuming the material to be all acid, its average molecular weight was 73 instead of 74, which it should be to be propionic acid. This is probably accounted for by the presence of some formic or acetic acid. About 3 per cent. of formic or 7 per cent. of acetic would be required. A solution was made up containing 0.025 per cent. of this material and 2.5 per cent. of lactic acid and compared with a solution having the same amount of lactic acid and 0.025 per cent. of acetic, by distilling over 125 cc. from 150. Titration of the distillates with 0.1 N NaOH gave the following figures: For propionic acid, 7.5, 7.7, 7.6; for acetic acid, 7.4, 7.6. From this it appears that the more rapid rate of distillation of propionic acid is offset by its higher molecular weight, so that if in determining volatile acid, some propionic is present and estimated as acetic, there will be no appreciable error in the figure for actual amount of volatile acid present.

Formic Acid.—A similar experiment was tried with C. P. formic acid, actual strength 86 per cent. A solution containing 0.025 per cent. formic acid and 0.25 per cent. lactic was distilled under the same conditions as above, the distillates taking 5.2, 5.5 and 5.6 cc. of 0.1 N NaOH. These figures indicate that when distillation is carried out in the manner described, if formic acid is present and is estimated as acetic, about 75 per cent. of it is accounted for.

Construction of Table for Volatile Acid.—Solutions were made up from the same C. P. lactic acid used in the first experiments, to which were added different proportions of acetic acid, so adjusted that the actual acetic acid amounted to the following percentages of the lactic acid used: One per cent., 2.5 per cent., 3 per cent., 4 per cent., 5 per cent. These mixtures were suitably diluted, and 150 cc. placed in the boiling flask of the standard distilling apparatus. The flame was regulated so as to give 125 cc. of distillate in about 50 minutes. After adding 125 cc. of water, the process was repeated, the distillates being titrated separately with 0.1 N NaOH. A series of experiments was

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tried with each mixture, and from the results a curve was made showing the relation of acid distilled over to acid present in the boiling flask for each strength, both for one distillation and for two distillations. It was found that the curve is a straight line for values of volatile acid above 0.5 per cent. The ratio of amount distilled over to total amount present becomes less as the proportion of volatile acid increases. When 1 per cent. of volatile acid was present, two distillations gave a total of 1 per cent. in the distillates. A part of this is lactic acid carried over. When the two distillates add up to 0.5 per cent. acetic, only 0.43 per cent. of acetic is actually present. When under the same conditions 5 per cent. is found, 5.5 per cent. is actually present. From these curves, tables were made, showing what per centage of volatile acid may be inferred from various amounts obtained in the distillate. These tables were merely tentative. A mistake was made in arranging them, which, however, does not affect the indications given by the work of the collaborators in regard to the practicability of the method. The fact of this mistake makes it not worth while to print the tables.

In relation to the behavior of volatile acids under steam distillation, see J. A. Wilson, "Rate of Distillation of Acetic Acid," *Journal of the Society of Chemical Industry*, vol 9, 1890, p. 18. Also H. D. Richmond in *The Analyst*, 1895, p. 193, 1906, p. 324 and 1908, pages 209 and 305.

Free Sulphuric Acid.

The method used by Harrison Bros. Co., Philadelphia, given on p. 47, January number of the JOURNAL, this year, was tested out. On a sample known to contain 1 per cent. H_2SO_4, it showed 0.98 per cent. It was found best, however, after adding alcohol, merely to heat to 60° C. and set aside in a warm place covered, instead of keeping on a water-bath for 2 hours before setting aside. This is to avoid as far as possible loss of alcohol, thus raising the percentage of water in the solution, and in the case of weaker acids causing a danger of redissolving some of the sulphates precipitated by the alcohol.

Free Acid and Anhydride.—The chairman tried many experiments in this connection, and is satisfied that the Besson method

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(p. 47) is dependable. A quantity of the sample containing about 0.75 gram of actual acid is diluted to about 50 cc. and at once titrated with 0.5 N NaOH and phenolphthalein to the first full pink. This titration, less an amount corresponding to volatile acid and sulphuric acid gives the free lactic acid. It is very easy, especially in the case of concentrated acids having high anhydride content, to pass the proper end-point. It is convenient to use for this determination 50 cc. portions of the dilution made up for volatile acid determination. After titrating one portion, a quantity within 0.5 cc. of the end-point may be run in slowly, so as to avoid error due to leaving solution on the sides of the burette, and then it is well to complete the titration by running in the alkali at the rate of 2 or more drops per second, stirring vigorously, and stopping as soon as the pink color spreads uniformly through the solution. All the titrations for free acid should be made as soon as possible after the solution is made up, as the free acid increases at the expense of the anhydride in the diluted solution.

When the first titration is complete, an excess of alkali is added, and the solution stood aside for 10 or 15 minutes at room temperature, to permit the anhydride to combine with the alkali. An excess of 0.5 N acid is then added, and the solution boiled and titrated back with alkali. The amount of alkali used by the anhydride is now obtained by subtraction, and figured to lactic acid. This result is called lactic acid equivalent to anhydride present in sample.

Samples.

Seven samples were sent out, numbered from 1 to 7. They may be described as follows: No. 1, manufacturer's sample, dark, 22 per cent.; No. 2, a mixture, made up of C. P. lactic acid, C. P. sulphuric acid 0.25 per cent., C. P. acetic acid 1.5 per cent. and C. P. propionic acid 0.5 per cent.; No. 3, manufacturer's sample, labeled "44 per cent. light refined"; No. 4, C. P. concentrated acid; No. 5, manufacturer's sample, labeled "22 per cent. light refined"; No. 6, manufacturer's sample, labeled "22 per cent. dark"; No. 7, manufacturer's sample, labeled "lactic acid 22 per cent." These were sent to Messrs. Orthmann, Faust, Carnell, and

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Reed, who had signified their willingness to do the work. Later, Messrs. Small and Fox responded, and samples were sent to them, but not enough No. 4 remained for a sample for Mr. Fox.

TABLE I.—VOLATILE ACID, PER CENT.

Sample.		A. C. Orthman.	F. H. Small and F. W. Ames.	W. C. Carnell.	W. A. Fox.	L. Balderston.
1	1 distillation	0.69 0.85	0.05	0.91 0.93 0.88	0.64	0.69 0.67
	2 distillations.....	0.77 0.77	0.05	0.87 0.89 0.88	0.62	0.66 0.65
2	1 distillation	1.77 2.23	2.11	2.31 2.41 2.37	1.86	2.05 1.92
	2 distillations.....	2.37 2.37	1.97	2.35 2.54 2.44	1.74	1.88 1.84
3	1 distillation	0.09 0.09	0.05	0.41 0.38 0.38	0.00	0.02 0.04
	2 distillations.....	0.31 0.25	0.10	0.57 0.43 0.56	0.00	0.03 0.05
4	1 distillation	0.26 0.17	—	0.54 0.62 0.57	—	0.00 0.00
	2 distillations.....	0.43 0.43	—	0.98 1.04 0.97	—	0.00 0.00
5	1 distillation	0.00 0.00	0.02	0.17 0.17 0.17	0.00	0.00 0.00
	2 distillations.....	0.00 0.06	0.04	0.27 0.26 0.26	0.00	0.00 0.00
6	1 distillation	0.26 0.17	0.22	0.35 0.31 0.31	0.10	0.15 0.15
	2 distillations.....	0.31 0.18	0.24	0.33 0.37 0.37	0.10	0.14 0.17
7	1 distillation	1.00 1.00	1.15	1.21 1.18 1.25	0.98	0.98 0.95
	2 distillations.....	1.46 1.34	1.07	1.19 1.21 1.23	0.92	0.93 0.92

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TABLE II.—FREE LACTIC ACID, PER CENT.

Sample	1	2	3	4	5	6	7
A. C. Orthmann	18.4	48.8	39.2	72.5	20.2	19.2	30.1
	18.3	49.0	39.0	72.3	20.1	19.4	29.8
	18.4	49.1	39.1	72.7	20.0	19.5	30.2
F. H. Small and F. W. Ames	20.6	51.2	40.1	74.4	20.7	19.8	31.3
	20.5	51.1	40.2	74.3	20.7	19.8	31.4
	20.6	51.1	40.2	—	20.7	19.8	31.4
W. C. Carnell	18.9	45.8	38.6	71.1	19.6	19.2	30.0
	19.0	45.8	38.5	71.2	19.6	19.0	30.0
	18.9	45.9	38.7	71.3	19.6	19.0	30.0
W. A. Fox	19.8	49.1	39.5	—	20.0	19.5	30.7
L. Balderston	19.2	45.3	39.3	73.3	19.8	19.6	29.9
	19.5	45.0	39.8	72.9	20.0	19.6	29.8
	19.4	45.0	39.3	72.4	19.6	18.7	29.8
				74.1[1]			

[1] After standing diluted four days.

TABLE III.—PER CENT. LACTIC ACID EQUIVALENT TO ANHYDRIDE.

Sample	1	2	3	4	5	6	7
A. C. Orthmann	0.6	3.3	2.1	13.5	0.8	1.1	1.5
	0.5	2.1	1.6	9.1	0.3	0.9	1.2
	0.5	2.2	1.4	9.1	0.5	0.9	1.0
F. H. Small and F. W. Ames	0.4	2.8	2.2	14.6	0.4	1.0	1.6
	0.5	2.9	2.3	14.6	0.4	1.0	1.5
	0.4	2.8	2.2	—	0.4	1.0	1.6
W. C. Carnell	0.4	4.8	1.8	9.8	0.4	0.6	1.6
	0.3	4.4	1.6	9.7	0.5	0.7	1.4
	0.2	4.7	1.6	10.1	0.3	0.7	1.3
W. A. Fox	0.3	2.6	1.7	—	0.3	0.8	1.1
L. Balderston	0.4	4.2	2.0	11.6	0.3	0.9	1.5
	0.7	5.3	1.2	12.4	0.3	0.8	1.3
	0.3	6.2	1.7	11.2	0.4	1.2	0.9
(Using the Harrison method)							
W. C. Carnell	1.9	6.5	5.5	16.2	2.4	2.3	2.7
L. Balderston	2.2	8.2	7.4	11.7	3.8	2.4	3.5

TABLE IV.—TOTAL LATIC ACID, FREE AND AS ANHYDRIDE.
(Sum of average values.)

Sample	1	2	3	4	5	6	7
A. C. Orthmann	18.9	51.5	40.8	83.1	20.6	20.3	31.3
F. H. Small and F. W. Ames	21.0	54.0	42.4	88.9	21.0	20.8	32.9
W. C. Carnell	19.2	50.5	40.3	81.0	20.0	19.7	31.4
W. A. Fox	20.1	51.7	41.1	—	20.3	20.3	31.8
L. Balderston	19.9	50.4	41.1	85.0	20.1	20.3	30.9
(Using Harrison method for anhydride.)							
W. C. Carnell	21.3	53.9	44.0	88.6	21.9	21.2	33.3
L. Balderston	21.6	53.3	46.9	85.1	23.6	21.7	33.3

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TABLE V.—FREE SULPHURIC ACID, PER CENT.

Sample	1	2	3	7
A. C. Orthmann	1.28	0.45	0.00	—
F. H. Small and F. W. Ames	0.86	0.36	0.00	—
W. C. Carnell	0.75	0.37	0.00	—
W. A. Fox	0.51	0.34	0.00	—
L. Balderston	0.67	0.31	0.00	0.20

DIRECTIONS.

The directions sent out described the distillation method for volatile acid as given below, the Besson method for free acid and anhydride, and the Harrison method for free sulphuric acid. Sulphuric acid was asked for only on the first three samples. The directions also included explanatory matter embraced in the pages preceding, the tables mentioned above, and a sample analysis, worked out in detail.

Results are given in the accompanying tables. On volatile acid one collaborator finds higher results in nearly all cases than the rest of the men. The cause of this difference has not been discovered. On free acid, several men get high results on No. 2, which may be due to titrating too slowly near the end or it may be because of gradual passing over of anhydride into free acid, since the sample was made up from a concentrated acid, and the work of the collaborators was done at different times. Those who have higher results on free acid have lower on anhydride, which is to be expected.

But little criticism or comment was furnished by the collaborators, except that Dr. Carnell objects to the Besson method for free acid and anhydride. He found different results due to varying periods of standing, and holds that the higher results (shown in the tables) obtained by the Harrison method are more correct, because the excess alkali does not completely take up the anhydride by standing a brief time at room temperature. He submitted a series of tests with C. P. acid, where the time of standing varied from 15 minutes to 2½ hours, and the anhydride figures ranged from 9.8 to 16.4 per cent. The chairman then weighed out 8 samples, and after making a first titration with 0.5 N NaOH in the cold, added 5 cc. excess, let them stand varying times, added 5 cc. 0.5 N H_2SO_4, boiled, and titrated back with 0.5 N NaOH. This last figure is called in Table VI

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TABLE VI.—FREE ACID AND ANHYDRIDE IN C. P. CONCENTRATED LACTIC ACID.

Grams of sample	First titration	Time of standing	Second titration	Per cent. free acid	Per cent. as anhydride	Total per cent.
1.007	16.1	10 minutes	2.9	72.0	12.9	84.9
1.029	16.4	20 minutes	3.2	71.7	14.0	85.7
1.026	16 5	20 minutes	3.4	72.3	14.9	87.2
1.007	16.0	30 minutes	3.2	71.5	14.3	85.8
1.084	17.4	40 minutes	3.6	72.2	15 0	87.2
1.182	18.9	50 minutes	3.2	71.9	12.2	84.1
1.101	17.5	2½ hours	3.7	71.5	15.1	86.6
1.005	16.0	2½ hours	3.4	71.7	15.2	86.9

"second titration." While these results show that the chairman finds difficulty in getting concordant results on C. P. concentrated acid, they do not show that long standing is necessary to get full figures for anhydride.

The results of the collaborators for the weaker acids are in fair agreement, and the chairman believes that the work of Dr. Besson, referred to in last year's report, makes it highly probable that the higher results obtained by the method used at Harrison's are due to the taking up of alkali by substances other than anhydride present in the crude acids. It seems unlikely at any rate that lactic anhydride which can only be made available by heating to the boiling point in the presence of excess of caustic alkali would be of much value to a tanner. In the chairman's experience, C. P. acid gives practically the same result by both methods, which seems to him to support Dr. Besson's contention.

RECOMMENDATIONS.

Volatile Acid.—It is recommended that the distillation method be adopted, using apparatus made up of a long-necked Kjeldahl flask, 300 cc., connected to a vertical spiral condenser through a Kjeldahl bulb trap, the total height from the bottom of the flask being from 20 to 24 inches. In order to make up a solution for distillation, weigh out about 1 gram of the sample, make up to about 50 cc. and titrate with 0.5 N NaOH; calculate the result to lactic acid, and on this basis make up a solution containing about 15 grams of acid per liter. Place 150 cc. of this dilution in the distilling flask and distill over 125 cc. in from 47 to 53 minutes, counting from the time the first drop falls into the receiver. Collect the distillate in a graduated cylinder. Add

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125 cc. of water to the residue in the flask and repeat. Titrate both distillates with 0.5 N NaOH and phenolphthalein and calculate results to grams of acetic acid. Convert these figures for acid found in distillates to actual weight of acid present in boiling flask by means of tables, and convert these results to percentage of acetic acid present in the sample. It is recommended that tables for this purpose be constructed from the collated results of experiments by several workers.

Free Sulphuric Acid.—The method recommended is as follows: Dissolve 50 grams of sample in alcohol, which should be neutral and at least 95 per cent. strength. Heat to 60° C., cover and stand aside over night in a warm place. Filter off precipitated material and wash with alcohol. Evaporate off the alcohol, make up residue to 250 cc. with distilled water, add 5 cc. strong HCl, boil, add $BaCl_2$ and determine $BaSO_4$ in the usual way. Calculate to per cent. H_2SO_4 on original sample.

Free Acid and Anhydride.—The method recommended is essentially that of Besson: Titrate 50 cc. of the solution made up for volatile acid, in the cold, with 0.5 N NaOH and phenolphthalein to first full pink. Call this figure "first titration." From it subtract a number of cubic centimeters 0.5 N NaOH equivalent to the volatile acid and sulphuric acid present in the 50 cc. of dilution. If HCl, oxalic or other free acid be present, deductions for these must also be made. Calculate the remainder to lactic acid and express it as a percentage of the sample. After completing the first titration, add 4 cc. excess alkali, or in the case of concentrated acids 5 cc., and stand aside at room temperature 15 minutes. Then add 5 cc. 0.5 N H_2SO_4, boil and titrate back with 0.5 N NaOH. The amount of alkali used by anhydride is now obtained by subtraction, and calculated to lactic acid. Express this as per cent. of lactic acid equivalent to anhydride present in sample.

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THE ANALYSIS OF MATERIALS USED IN CONNECTION WITH BEAM-HOUSE PROCEDURE.

Committee Report.

By Charles R. Oberfell, Chairman.

It was thought desirable by the Chairman of this Committee to review the methods which have been proposed by individual workers for the analysis of materials used in connection with beam-house procedure, thereby gathering together, sifting out and classifying these proposals for subsequent collaborative work if it is thought necessary.

After a review of the literature it was found that in reference to those methods dealing with the actual removal of the hair that the report of the I. A. L. T. C. Committee in 1912 covered the field thoroughly, and their recommendations, subsequently adopted, are similar to those here set forth.

The following items demand attention for a complete scheme of analysis of lime liquors. Lime liquors as here used comprising straight limes and mixtures of lime and sulphides.

Filtration.
Total alkalinity.
Total and caustic lime.
Ammonia.
Caustic alkali.
Sulphides.
Dissolved hide substance.

The influence of the very small particles of lime on the estimation of the above items presents the necessity of deciding to what extent the liquor shall be filtered. It is obvious that for total alkalinity all of the lime particles shall be absent, this may be accomplished by filtration through a grade of paper made to retain the finest precipitates. If sufficient of the lime particles are present in the liquor they will form a film on the paper which then gives an optically clear filtrate. In the estimation of the ammonia where the lime particles have no direct bearing, simple filtration through cotton or glass wool is sufficient. Stiasny recommends centrifuging the liquor to be Kjeldahled for nitrogen, however, this has no real advantage over clear filtration.

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Stiasny has found that kaolin does not give satisfactory results in filtration.

Methyl red has been proposed as preferable to phenolphthalein or methyl orange as an indicator in the determination of the alkalinity because it gives a sharper end reaction. Phenolphthalein is not sharp in its end reaction but it has the advantage of estimating only the stronger bases; methyl orange is quite indistinct in its color change and is sensitive to both the strong and weaker bases. Both phenolphthalein and methyl red are useful no doubt. Phenolphthalein serves a useful purpose in that after an estimation of the total alkalinity using it, the alkalinity due to sulphides and ammonia as found by other methods may be subtracted, thus giving the alkalinity due to caustic lime alone. Total lime may be determined gravimetrically and the difference between total CaO and caustic CaO represents the lime-nitrogen and lime-ammonia complexes. There has been no reasonably satisfactory method proposed for the determination of the caustic alkali in these liquors.

The estimation of ammonia has been greatly improved by Procter's proposal that magnesia be used to decompose the ammonium salts, since its solubility is so small that no appreciable hydrolysis of organic matter takes place. It is therefore more accurate and consumes less time than any of the other distillation methods or the Schloessing method. No filtration of the lime liquor is necessary.

The most convenient method for the determination of sulphides and the one which alone has survived the test of constant usage is that based on titration with zinc sulphate solution, as first proposed by Procter. The original solution contained zinc sulphate to which was added sufficient ammonia in excess to just dissolve the precipitate of zinc hydroxide formed. Blockey & Mehd (A. L. C. A. JOURNAL, 1912, p. 358) showed that the zinc was also precipitated as hydroxide from this solution as well as sulphide when added to the lime liquor, and proposed the use of ammonium chloride in addition to the ammonia to prevent this precipitation, and using sodium nitroprusside as an external indicator.

The amount of dissolved hide substance which a lime liquor

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contains is of prime importance, its estimation by the determination of the total nitrogen by Kjeldahling the filtered liquor is somewhat time consuming and is a hindrance in control work. What is desired is a quick easy method for total hide estimation. Of course the total hide as found in this manner is not derived wholly from leather forming materials, but some is caused by solution of the epidermal and interfibrillar substance. In order to make a saving of time in this total nitrogen determination by eliminating the ammonia distillation Bennett (A. L. C. A. JOURNAL, 1909, p. 140) proposed the addition of formaldehyde after neutralization of the digested solution, whereby the formaldehyde condenses with the nitrogen of the ammonium sulphate to form hexamethylenetetramine, releasing for titration of an equivalent amount of sulphuric acid. The writer on investigating this proposal on lime liquors obtained the following results in comparison with the distillation of the ammonia.

	Milligrams nitrogen per 100 cc. lime liquor.			
	Kjeldahl method.		Formaldehyde method.	
Liquor.	1.	2.	1.	2.
No. 2	—	63.88	59.95	60.37
" 3	60.65	60.93	63.88	58.97
" 4	46.89	46.89	44.65	43.52
" 5	46.05	45.91	43.66	42.12
" 6	35.52	—	32.29	30.88
" 7	89.72	89.50	87.05	85.64
" 9	83.81	84.38	81.43	81.85

The formaldehyde method gave uniformly low results and it is difficult to get agreement in duplicates.

Various methods have been proposed for estimating the hide substance besides the Kjeldahl method, to be used for control purposes. Some of these proposals may be reviewed.

Precipitation Method.—After neutralization of the lime liquor the dissolved hide is precipitated with a saturated sodium chloride solution and the volume of precipitated hide measured. This method is extremely rough and it has been found that about half only of the total hide substance is removed from solution.

Bennett's method consists in titrating 25 cc. of the filtered liquor with acid, using first phenolphthalein as indicator and when the color is gone adding methyl orange and continuing the titration to the final change. The difference in the acid required

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by the two indicators being due to the weak bases and represents a measure of dissolved hide. Various investigators have been unable to confirm the constant factor claimed by Bennett, moreover it fails in the presence of alkali sulphides.

Eitner's method consists in precipitating the lime in a measured quantity of the filtered liquor with carbon dioxide, collecting on a tared filter, washing with water and dilute hydrochloric acid, and weighing after drying at 100° C. as "dissolved hide substance in combination with lime." The filtrate is precipitated by acidifying with hydrochloric acid, the precipitate washed, dried and weighed as "organic substance uncombined with lime." Procter considers the distinction doubtful and states that this method does not include all organic products present, especially the amines and amino-acids.

Trotman and Hackford proposed acidifying the hot filtered lime liquor and saturating with zinc sulphate which precipitates albumoses. The peptones in the filtrate are precipitated with tannin, filtered and the nitrogen determined by Kjeldahling, the factor for conversion of nitrogen into peptones being 5.42. This method does not facilitate matters much and the distinction is arbitrary.

Procter's tannin precipitation method only removes a portion of the dissolved hide substance, but the method may be of value as indicating that proportion of the dissolved hide which if left in the skin would have been formed into leather.

Stiasny's method differentiates the various forms of decomposed hide substance and is based on the reaction observed by Schiff that amino-acids by condensation with formaldehyde are increased in acid character:

$$R\begin{cases} -NH_2 \\ | \\ CO.O \end{cases} + CH_2O = R\begin{cases} N = CH_2 \\ \\ COOH \end{cases} + H_2O.$$

There are many representatives of the amino-acids in soak and lime liquors formed by hydrolysis of the albuminoids of the hide, and the analytical principle for the determination of the extent of this hydrolysis is by titration before and after addition of formaldehyde. The ratio of the results for total nitrogen and this titration difference expresses the degree of hydrolysis.

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Where sulphides are present the addition of iodine to the liquor is required, this having replaced zinc sulphate which was found to partially precipitate dissolved hide. The factor expressing the degree of hydrolysis is given by the formula N/C where N is the number of milligrams of nitrogen found in a definite volume of liquor and C the number of cubic centimeters of N/5 sodium hydroxide required to neutralize the same volume of liquor, after the addition of formaldehyde to the neutral liquor.

Stiasny has found the factor for gelatine to be 178 and the factor for the final hydrolysis product of hide, ammonia, to be 2.8. Any intermediate factor between these two may be calculated to express percentage of hydrolysis undergone. If for example the factor N/C equals 20.8 the percentage hydrolysis will be $\frac{2.8X + 178(100 - X)}{100} = 20.8$, where X equals the unknown percentage or in this case 89.7 per cent.

Unfortunately none of these methods distinguish that portion of the products derived from epidermal matter and that from the leather making fiber itself, they are only of value for empirically judging the condition of a beam-house where the values have been collected over a considerable period of time.

The following methods can be proposed as the most suitable for the determination of the items discussed.

The sample shall be drawn immediately after plunging or other suitable mixing of the vat or paddle and placed in a stoppered bottle. When filtering shake the contents of the bottle thoroughly just before throwing onto the filter so that the lime particles will form a filtering film on the paper. Keep the funnel and collecting receptacle well covered to prevent carbonization.

Total Alkalinity.—Pipette 25 cc. of clear filtered liquor into a porcelain dish of suitable size and titrate with N/10 acid, using either phenolphthalein or methyl red as indicator.

Total Lime (CaO).—Evaporate 50 cc. of the clear filtered liquor to dryness, ignite to destroy organic matter, redissolve in hydrochloric acid and precipitate the calcium as oxalate. Wash free from excess oxalate on a filter, dissolve the calcium oxalate in dilute sulphuric acid and titrate with standard potassium permanganate at 70° C.

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Caustic Lime (*CaO.*).—Subtract the alkalinity due to sulphides and ammonia from the total alkalinity as determined when using phenolphthalein as indicator.

Ammonia.—Use the clear filtered liquor or as filtered through a plug of cotton. Place 100 cc. in a distilling flask with several drops of methyl red and add dilute hydrochloric acid until the indicator just changes color. Considerable excess of magnesia is then added and the ammonia distilled off in the usual manner into a quantity of standard acid and finally the excess of acid titrated. Frothing may be prevented by adding a few drops of oil of turpentine.

Sulphides.—A N/10 solution of zinc sulphate is prepared by dissolving 14.38 grams of crystalized salt in water and adding ammonium hydroxide until the precipitate which forms is just dissolved and then adding 50 grams of ammonium chloride, and making the volume up to 1 liter. 25 cc. of the clear filtered liquor it titrated with this solution using a 0.2 per cent. solution of sodium nitroprusside on a spot plate. A drop of the solution is removed from time to time as the titration proceeds and added to the indicator. When a coloration no longer appears the reaction is complete.

Total Nitrogen.—20 to 50 cc. of the clear filtered liquor is made slightly acid with sulphuric acid and then concentrated in a 500 cc. Kjeldahl flask. 15 to 20 cc. concentrated sulphuric acid and 10 grams powdered potassium sulphate is added, then digested well until colorless. The ammonia is distilled off as usual into standard acid and the excess of acid measured with standard alkali.

Hydrolyzed Hide Substance.—50 cc. of the clear filtered liquor is neutralized with 10 per cent. acetic acid, using phenolphthalein, and approximately N/10 iodine solution added until a slight excess is present as denoted by the color. N/5 sodium hydroxide is then added till the phenolphthalein is reddened and after adding 10 cc. neutral 40 per cent. formaldehyde solution the titration is finished with N/5 sodium hydroxide. If the formaldehyde solution is not neutral it may be shaken with barium carbonate and filtered.

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Soak Liquors.—Soak liquors present no difficulties nor do they require special methods. The amount of dissolved hide may be readily determined by Kjeldahling. Where hydrolytic products are desired Stiasny's formaldehyde method as described for lime liquors applies. Any caustic alkali can be determined direct by titration and sulphides by the zinc sulphate method previously described. Sodium chloride may be estimated as in water analysis, the solution first being made neutral by the addition of a slight excess of acid and subsequent addition of magnesia.

Drench, Pickle and Deliming Liquors.—These require no special methods other than those always available.

Bates and Puers.—Little can be done in the way of chemical control of pure and bate liquors as the processes are complicated and largely bacteriological.

NIGERIAN AND SOMALILAND LEATHER.*

By Alfred Seymour-Jones.

Despite the fact that Nigerian leather has been exported to Europe and Asia from very early times—and it must take rank among the earliest of the known leathers—practically nothing is known regarding the origin of the raw skins, their preparation, tanning and dyeing, although the early travellers in West Africa make occasional references to the leather produced in Bornu and Kano. Nevertheless Nigerian leather has for ages been produced in much the same manner as it is to-day, and has been carried by camels across the deserts from Northern Nigeria to Tripoli, whence it has been shipped to overseas markets, or consigned *via* the Sudan to the markets of the East.

A typical caravan from Kano, in Northern Nigeria, to Tripoli, comprised "1,220 camel-loads strong, consisting of 200 loads of feathers, 1,000 loads of skins, and 20 loads of ivory." This caravan took 11 months to make the journey, and the cost of transport amounted to £27 per ton.

Since the British occupation of Nigeria the productive value of the native leather for export purposes has received considerable attention, and in due time it is anticipated that instead of the bulk

* *Leather Trades' Review*, March 17, 1915.

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of the exports being conveyed by caravans, the cheaper and quicker transport to the coast by means of rail and waterways developed by the British, will appeal to the native shippers.

It is by no means easy to convey an adequate idea of the annual trade in hides and skins from Northern and Southern Nigeria (these two areas are now amalgamated and called "Nigeria"). In the Northern area it is impossible to state with accuracy the total trade in the products, as the official returns only include those exported through certain of the southern frontier stations. Further, some skins are exported every year by the old caravan route across the Sahara to Mediterranean ports, and these are not included in the trade returns. The majority of hides and skins exported from Southern Nigeria are conveyed to the coast ports from the northern territories. The following are the exports recorded for the years 1910-1913:—

EXPORTS FROM NORTHERN NIGERIA.

Skins	Number			Value		
	1910	1911	1912	1910 £	1911 £	1912 £
Via Idah station ...	94,425*	164,533*	234,641*	4,609	8,177	13,595
Via Offa	—	9,060†	39,977*	—	1,053	1,003
Via Bude Egba	—	18,331†	—	—	467	—

* Dressed skins. † Skins and hides.

Hides	Number			Value		
	1910	1911	1912	1910 £	1911 £	1912 £
Via Idah station ...	22,007	25,738	52,639	605	3,326	8,887
Via Offa	—	—	73,951	—	—	5,418

N. B.—Separate figures for 1913 are not recorded for Northern Nigeria.

EXPORTS FROM SOUTHERN NIGERIA.

Year	Raw hides and skins		Tanned hides and skins	
	Number	Value £	Number	Value £
1910	54,633	8,899	120,967	6,000
1911	133,394	27,628	198,557	10,541
1912	316,188	51,161	496,950	17,671
1913	473,445	116,414	654,523	30,800

The Imperial Institute, to whom I am indebted for the foregoing statement and figures, adds, "As explained above, it is probable that these Southern Nigerian exports include those from Northern Nigeria quoted in the first two tables." What will doubtless appear to the reader is the immense increase in the

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number of skins and hides—both tanned and raw—shipped from all stations and ports in the four years enumerated, which would indicate Nigeria to be a country with a potential hide and skin supply.

An unsatisfactory economic feature is the price paid to the native for hides and skins. If any of the figures are taken it will readily be seen that during the four years given—a period which covers an almost unprecedented rise in hide values—the price of the raw skin or hide has scarcely varied; in the case of the tanned skin there is an actual decrease of value. Considering the importance of this phase of the question in its general economic relation to one of the youngest members of the British Empire, it is to be hoped that the Nigerian authorities will give it the fullest consideration.

Captain Orr in his book, "The Making of Northern Nigeria," says:—"The skins can be bought in Kano and Zaria at prices varying from 6d. to 9d., and as bookbinders are prepared to give as much as 6s., or even more, for a good specimen, there is room for considerable profit."

In regard to the supply of hides from Fulani cattle, Mr. E. D. Morel states in his book on "Nigeria":—"There would seem to be a future for a trade in hides, especially if Kano became the slaughter-center for cattle for the southern markets. The possible obstacle to this is partly political and partly enthological, and the first, at least, is worthy of special attention on the part of the Administration. Virtually all the herds in the Hausa States are the property of the Fulani. The Fulani is very fond of his cattle. He does not breed them for slaughter, but because he literally loves them. He knows every one of them by name, and lavishes as much attention upon them as he does upon his children. This is peculiar to him not in Nigeria only but all over Western Africa. Often have our officers in Northern Nigeria found it impossible to resist the pitiful appeal of tears for the restitution of a favorite ox or heifer taken with other under the 'jangali' (cattle tax) assessment."

The conversion of hides of cattle into leather does not appear to be so considerable an industry as that of the skins from sheep and goats. The latter owe their prestige in no small measure to the

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unqualified approval given to Nigerian tanned skins for bookbinding by the Committee of the Society of Arts for Bookbinding (see *Journal of Soc. of Arts,* July, 1901, and final report, 1905). This leather withstood all the tests applied by the members of the leather section, and so much were they interested in this leather that it was a matter of regret on their part that they were then unable to describe its manufacture. As a member of that committee, and responsible for the tests applied, I have never ceased to take the deepest interest in securing information regarding the Nigerian methods of tanning, etc., and the results of assiduously collecting material from all available sources are collated here. The facts will be found of more than ordinary interest to a wider circle than that represented by the theoretical and practical tanner with his claims for modernism in thought and application.

The African area embraced between latitude 5° to 15° north of the equator is a populous land which stretches from Sierra Leone Coast to Somaliland, and rich in animal and vegetable life and minerals. For thousands of years a comparative form of civilization has prevailed, which developed certain arts and crafts to a level of perfection unsurpassed in Europe until the 19th century. For example Kano has spun the finest cotton yarn, woven and bleached the finest cotton cloth, and exported them to distant lands for several thousands of years. In this area, too, the native has been preparing and tanning "Marocco" skins for ages without alteration in his methods; sending them across deserts and swamps to clothe the feet of Egypt's Pharaohs. From their cotton sheetings were made the white "tobes," or long white sheets worn by the natives throughout Northern Africa. When a harder wearing tobe was required, the leather manufacturer produced beautifully white leather as soft as a kid glove, or if the native demanded it, dyed. Then the color mostly in vogue was a dark maroon, this dye being obtained by digesting the bark of certain acacias. These leather tobes, fringed with finely plaited leather strips, may be seen to-day on festive occasions.

It must come as a shock to the modern producer of morocco leather to find the quality of his goods surpassed by the native leather of Nigeria, and if he be wise he will revert to the methods

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of his forefathers, which were not so far removed from the Nigerian operations or methods of procedure as may be supposed.

The native leather produced within the zone above outlined consists in the main of the skins from goats and sheep. The chief centers of the tanning industry are the provinces of Bornu and Kano in Northern Nigeria, with Kano City as the principal market. The preparation of leather is in the hands of the Kanuri, natives of the Bornu Province, and the Hausas, while the "trading" is mainly in the control of Arabs (Tripoli), whose biggest market is the United States of America, while a modicum goes to France, Italy, Austria-Hungary and Great Britain.

It has been stated that sheep only form 20 per cent. of the skins exported, but this is merely guess work, because (*a*) the sheep and goat skins are not separated for export purposes, (*b*) the two are so intermixed and similar in characteristics as to make it extremely difficult even for an expert to say which—after flaying and trimming.

Taking the tanned Niger skins in bulk lots, the goat skins undoubtedly predominate, although there are many skins which raise a doubt in the minds of experts as to whether they are sheep or goat. There are several tests which may be applied as a guide, a portion of a tanned skin may be grained when the contour of the grain thrown may decide the point, although failure may occur owing to the tightness of certain doubtful skins. Examination with a magnifying glass is an aid, but inconclusive. A sloping section may be cut, as detailed in my work "The Sheep and Its Skin," and this is a more reliable guide in the hands of an expert, but the less experienced must rely upon the general appearance and characteristics of the skins.

The reason for this difficulty is due to the following facts: The Nigerian long-legged sheep (*Ovis logipes carnapi*), according to Lydekker in his book "Sheep and its Cousins," are typically characterized by the great development of the throat-fringe of the rams, the strongly pronounced Roman profile of the entire head, the long drooping ears, the presence of a pair of hairy cylindrical tags or lappets on the throat, the slender elongated limbs, the hairy tail which reaches below the hocks, and the rather long shaggy coat, marked with blotches of black, brown,

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or fawn on a glistening white ground. Whereas the ears of the rams are completely pendant, those of the ewes are stated to be in some cases directed partly outwards. The rams alone have horns, which are of considerable length and directed almost immediately outwards; these, when fully developed, making about one complete turn. Not infrequently the head, with the exception of the muzzle and forequarters, are black, while the remainder of the body is white; but there is considerable variation in this respect, and in some cases the head is mainly white with a large black patch on each side enclosing the eye. In some instances the throat-tags may be absent.

From the foregoing description it will be observed that this breed of sheep cannot be classed among the wool-bearing variety, but is a true "hair sheep." This long-legged breed (*Ovis logipes*) was domesticated during the Neolithic age, when the use of metal was unknown, and the sister breed which inhabits the other areas of Central Africa and resembles the Nigerian breed very closely, is only distinguishable by its inferior size of body. The skins are likewise converted into leather by the natives, even so far as Somaliland, and there can be little doubt that many of them find their way into the markets as competitors with Niger leather. It will, therefore, be interesting to narrate and compare the methods of Somaliland with those of Nigeria, in so far as the former are known.

In the past the Niger-tanned skins have come to the European market dyed, but left more or less in the rough as regards any pretence to finish. The prevailing colors were red to a reddish brown, green to a greenish blue, and a small quantity of yellow or buff—clearly showing the difficulty in obtaining regular shades. The general run of the skins, so far as treatment resulting from tanning is concerned, leaves much to be desired in the matter of regularity. Some of the skins will be fully tanned, and would do credit to, and compare favorably with, the best European productions in a similar line, but the bulk falls far short of the bookbinder's demands. Some are under-tanned; others are hard down the mane, due to excess of fat present; while others are too tight or too thin and hard. It is evident that the bulk of the Niger skins must be re-processed by the European

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tanner before they are acceptable to the bookbinder. This re-dressing is not always carried out to the advantage of the skin, and, further, it should be borne in mind that a skin once tanned may be compared with a piece of good steel, the repeated heating and cooling of which spoils its temper. As a rule, re-tanning does not improve an already tanned skin. It therefore behooves the Nigerian Administration to make some attempt to educate the Nigerian tanner and to show him how to avoid his mistakes. This may be done by a tactful man who knows his trade, and who, while informing the native as to the right road to travel, will see that he does not upset time-honored methods. It may be difficult to obtain an instructor who can devise methods to meet the many obstacles such as are produced by climatic conditions, but with the help of the local scientifically trained men in the Administration, the difficulties might be overcome.

Many writers who have visited Nigeria state that efforts are being made to create an export trade in undyed Niger-tanned skins. Everyone will agree that this is a wise move, because it will increase the market for these skins, which can then be dyed to the buyer's own shades. That this movement is meeting with some success is proved by the fact that more Niger skins are coming to this country in the "crust" condition.

The importance of the Niger leather trade to the white race in general is such as to warrant greater attention at the source of production than it has hitherto received. The native demand is small, being confined to articles of dress (like tobes), pillow covers saddlery, etc.; in other words, whereas the local demand is limited, the supply is great, and with the increased transport facilities, bringing Nigeria into more rapid and cheaper communication with the buyer, the British leather men will be well advised to turn their attention to the potential hides and skin supplies of Central Africa, and especially of the area under review.

The Preparation of Niger Leather.

The information upon which the foregoing and the following matter is based has been collated from the reports of Mr. Dudgeon (superintendent of agriculture for the West African Colonies and Protectorates), Mr. Gowers (resident of Bauchi Province),

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Mr. Hoffmann (British Cotton Growing Association at Oyo, Lagos), Dr. D. Alexander (Government medical officer in Northern Nigeria), The Imperial Institute (South Kensington, London), Captain C. W. J. Orr ("The Making of Northern Nigeria"), Dr. Ralph E. Drake-Brockman ("British Somaliland"), Mr. E. D. Morel ("Nigeria"), and from scattered references in Colonial reports and journals.

The methods of treatment followed by natives of West Africa agree in general principles but vary in details, according to the district. The operations divide themselves under the usual heads—(*a*) depilation, (*b*) bating, (*c*) tanning, (*d*) dyeing. The tools employed are crude, and the vessels are large earthenware pots. The tanning industry is widely distributed, and may be said to be almost a household occupation, but only in the sense of implying the extent to which the people follow that occupation and the relative smallness of each individual output.

On the skins being received from the local butcher they are in some instances washed, after which they are treated to an alkaline bath which compares with the modern method of liming. In some districts this bath is simply a mixture of wood ashes and water. According to Dr. Alexander, the Kanuri and Hausas, who are important producers of Niger leather, employ a strong alkaline preparation known as "toka," which consists of the ash obtained by burning the wood of the "Merki" (probably *Anogeissus leiocarpa*) or the "Anum" tree, or by burning the vegetable and other refuse from tanning and dyeing pits with wood from Merki, Anum, or Karumga (*Acacia Seyal*) trees.

A sample of "toka" has been analyzed by the Imperial Institute with the following results:

	Per cent.
Lime, CaO	18.45
Magnesia, MgO	2.03
Ferric oxide and alumina, Fe_2O_3 and Al_2O_3	7.79
Silica, SiO_2	65.96
Sulphate anhydride, SO_3	0.22
Phosphoric anhydride, P_2O_5	0.86
Carbon dioxide, CO_2	2.09
Water, H_2O	2.12

No organic matter was present, and the silica occurred almost entirely as sand. "Toka" is, therefore, very largely quicklime

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mixed with sand and other impurities, and its use as a depilatory corresponds with the similar use of lime in European tan-yards.

The liming or depilatory process is carried through in the space of 24 hours, and the hair is scraped off with a blunt knife.

In the Ingra, Bobi and Kontagora districts of Northern Nigeria the depilation process assumes an interesting phase. Usually the skin is pegged and dried, yet it may be treated in the fresh condition. It is then placed in a calabash containing water and the powdered pods of an acacia, and left there for three days, after which it is removed, pegged out on a board and scraped with a bent knife until all the hair is taken off. The skin is then permitted to dry, and when finished is of a pearly white color.

Apparently this is the method of producing the white skins for making "tobes" already referred to, as the three observers, Messrs. Dudgeon, Hoffmann and Gowers, all agree that the tanned skin is next oiled by rubbing in either palm oil, ground nut oil or shea butter, the skins being meanwhile rubbed and pulled by hand until it becomes quite soft, when they are ready for dyeing.

It will be obvious to all practical men that this description cannot apply to what is generally known as "Niger leather." As the foregoing method somewhat resembles the principles of chamois-leather making, it is desirable to have further knowledge of this production.

In consequence of the climatic conditions of West Africa, it is evident that some action other than alkaline plays the principal part in depilation. If similar skins were immersed in European lime liquors, they would take many days to depilate. It appears to be a clear case in favor of the bacterial theory as the chief agent in depilation. As the immersion accomplishes the act of depilation only and the skins are not returned to the lime liquor as is the case in Europe, the problem of swelling the skin in subsequent liquors in order to loosen the fiber, plays no part. After depilation "they are allowed to dry for a day," when they are ready for bating. This repeated reference to drying appears to be the natives' method of sterilizing the skin between operations while the skin is in the pelt condition.

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Somaliland Methods.

Before proceeding with the West African processes of leather manufacture, it will be of interest to retail something of the modes of collection and sorting of skins on the East Coast. Dr. Drake-Brockman records the following notes: "In Somaliland hides and skins, especially the latter, form the main exports. The method of skinning the animals and drying their skins adopted by the Somalis, in the case of both sheep and goats, is the same; the skin is not cut longitudinally down the middle line, but literally peeled off the carcass from behind forwards, after the legs have been freed; it is then neatly folded lengthwise and pegged out to dry. When folded in and dried in this manner, the skins can be packed together in neat bundles for export. As may be imagined, the butchers' skins, or in other words, those prepared at the coast, are usually found to be superior to those coming from the interior, owing to their being not only better pegged out and dried, but to their being less frequently handled. The best sheep skins are to be bought at Bulhar; they are said to be superior to those exported from either Berbera or Zeyla. Skins from the Ogaden country are, as a rule, inferior, owing to their being too dry, improperly stretched, and of inferior consistency. On the other hand, those from Burao and Jig-Jigga are usually large and of good quality, and can be recognized by the expert trader owing to the reddish tint about them, due to the red soil of the Haud. Skins taken from animals during and immediately after the rains, when the animals have had plenty of green grass to eat, are never as good as those obtained during drier months of the year. Each skin is bought separately at the coast, after it has been carefully examined for flaws and weighed. When collected in the warehouse the skins are again individually examined for flaws and weighed, being finally done up into bundles according to their weights. A sheep skin rarely exceeds 3 pounds in weight, while all over 2 pounds are good. The usual method of classifying sheep skins is as follows:

1. First quality. Skins possessing no flaws.
   - (*a*) 100 skins weighing not less than 200 pounds.
   - (*b*) 100 skins weighing not less than 170 pounds.

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(*c*) 100 skins weighing not less than 140 pounds.
(*d*) 100 skins weighing not less than 125 pounds.
(*e*) 100 skins weighing not less than 100 pounds.
(*f*) Lamb skins.

2. Second quality. All skins possessing defects:
(*a*) 100 skins weighing from 125-170 pounds.
(*b*) 100 skins weighing from 125 and under.

Goat skins are generally classified as follows:

1. Skins without flaws.
(*a*) Heavy. Those weighing 1½ pounds or more.
(*b*) First quality. Those weighing 1 pound or more.
(*c*) Medium. Those weighing ¾ pound, such as the skins of kids.
2. All skins under ¾ pound in weight.
3. All skins possessing defects.

Numerous are the causes giving rise to defects in skins, the chief among them being branding-marks, scars following burns, and other injuries, skin diseases, etc.

The greater portion of the Somali sheep and goat skins find their way via London to America, where they are classified as "East Africans," and are almost entirely used in the manufacture of gloves at Gloversville, N. Y., U. S. A.

In the production of leather the Somali closely follows the lines of his western colleague. The skin is first soaked in water for 12 hours; it is then taken out and put into a solution of lime and water for another 12 hours, or for such time that the hair can be easily scraped off. Then it is washed again (this is not necessary), before being placed in the freshly prepared "watta" solution, which is not unlike tea in color. In this it is left from 24 to 48 hours, according to the strength of the solution, after which it is pegged out to dry. Dr. Drake-Brockman makes no reference to bating, but it is possible that this watta solution may have been mistaken by him for a sour bate, similar to that prepared from babool pods in India.

Bating and Drenching in Nigeria.

The several observers either record the use of processes which are very similar to those already known and practised in Europe,

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or they fail to note whether bates are used or not. The latest and most complete report is that of Dr. Alexander, who gives the interesting information that the natives of Kanuri employ the excreta of the "Kairo" bird (*Pyromelana afra*), or, if this is not obtainable, the excrement from domestic fowls; should the supply of either of these fail the husks of guinea corn heads, known as "dousa" are used. The Hausas do not use excretas, but make a drench of the "dousa" husk (bran).

The disclosure of the foregoing facts show how closely the Nigerian methods of bating correspond to those employed in Europe and America, and with the "bran-drench" or bate which has been employed in Egypt and India since time immemorial.

Gowers refers to an "aqueous decoction of the stem of a plant known as 'Serri,' presumably also utilized as a bate. This 'Serri' has not yet been identified."

After bating, the skins are scraped (scudded?), rubbed, and pulled until they are thoroughly soft and pliable, when they are ready for tanning. No attempt seems to be made to extract the fat from the necks or butts, where it may have accumulated in excess. This accumulation is a serious matter in certain of the heavier types of sheep throughout the collecting area, and if not removed it causes the fatty parts to resist the tannin, resulting in a horny leather when dried.

Tannning in Nigeria.

Throughout Nigeria the pods of the *Acacia arabica* are the chief tanning agent. In one instance I find it is employed in a similar manner to a bate, as is the custom in India. These pods are locally known as "gabarrua" or "baggarua," and when exported are called "Gambia pods." In the Sudan they are called "Sarri" (this is probably the same as "Serri" mentioned by Gowers). It is also probably the same as "Bonni," which is referred to by Hoffmann in his account of Oyo tanning.

The bark of the *Acacia arabica* does not appear to be used as a tanning material, and perhaps the reason for this may be found in its low tannin content compared with that of the fruit (pod). The bark yields a true catechol tannin of from 12-20 per cent. (Procter), whereas the pods contain 26 per cent. in a Nigerian sample to 35 per cent. in a Sudan sample (Imperial In-

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stitute). If the native preference for the pod be due to tannin strength the selection is interesting, but I incline to the opinion that the Hausas should be credited with a great power of observation and deduction. Apart from tannin strength he has probably observed that the bark did not produce sound leather, *i. e.*, the leather became extremely dark and red under the influence of the tropical sun during drying. This change would in itself be fatal to his final operations when producing pale or gaudy colors. On the other hand, he would find that the pods, when digested and used as a tan liquor, produced a soft and white leather which was practically uninfluenced by the sun's rays. "The tannin of the pod is allied to divi-divi, which is not precipitated by lime water" (Procter).

Somali Tanning.

"Tanning is done entirely with the native tanning barks and leaves, and the three commonly used for this purpose and recognized as the best are, in order of their superiority, the leaves and tender young branches of the watta bush (*Osyris abyssinica*), the 'thai' or bark of the root of a species of acacia known as galol, and the bark of another acacia called marra. The watta is by far the best and colors the leather but slightly, whereas the other two, and more particularly the marra, color the leather a deep reddish brown" (Drake-Brockman).

No methods for reducing the skins in substance akin to shaving, or that of striking or setting out the skin to get out the stretch, seem to have been devised by the natives. The nearest approach to the latter operation is that of pegging the skin out.

Before drying, those skins intended for dark colors receive a coat of oil, such as ground nut, palm or shea butter, but skins required for light colors, such as yellow, buff, etc., are not oiled.

Dyeing of Nigerian Leather.

Most of the skins which reach Europe from Nigeria are dyed, and are chiefly of a reddish color. This shade, or, to be accurate, these shades—for their number is legion in Niger leather—are produced from a variety of sorghum known as "Karrandeffi," of which only the stems are used. It has not been identified botanically, but is identical with the Sudanese dyestuff known as

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"Sikhtyan" and used for leather dyeing. This "Sikhtyan" from the Sudan was examined for the Imperial Institute by Mr. A. G. Perkin, F. R. S., who states that it is a substantive red dyestuff of the same type as camwood, red sandalwood, and barwood, all of which are supposed to contain the same red dye called "santalin" or "santalic acid."

Sorghum or "Karrandeffi" stems are pounded up and treated with an aqueous solution of "potash," when a brilliant, almost crimson, liquid is obtained, which is rubbed into the skin until the latter acquires the desired tint. The skin is finally washed with water to which a little lime juice has been added, and, after drying in the sun, is ready to be packed for export.

The making of "potash," according to Drake-Brockman, follows very elementary lines. The salsol bark, which so freely grows around Bulhar (Somaliland), is often collected and burnt for the potash it contains; after burning it is then treated with water and boiled, or merely left in a basin in the full blaze of the tropical sun, when it will be found that the potash crystallizes out. Presumably the method follows the immemorial methods of collecting sea salt.

The same writer mentions that the young shoots of the salsola are also gathered, together with the *Cressa cretica,* a small plant with mauve or lavender-colored flowers called "Naggard ad," and burnt together, and the ashes stirred up in water to form a solution for the purpose of staining leather.

Captain Orr states that the Nigerians usually employ juice extracted from the stalks of the holcus for dyeing their leather, which gives them a rich red color. This holcus is most probably identical with sorghum or karrandeffi, a variety of cane-like grass. Camwood, which is abundant in West Africa, is likewise used for dyeing red shades. In all cases the natives are reported to employ the local "potash" known as "kanwa," or "toka" (see earlier note) for preparing the red-dye bath. Dr. Alexander states that the Nigerian "potash" or "kanwa" is a mixture of sodium bicarbonate and sodium carbonate, and closely resembles the composition of the mineral "trona," which is found locally. Turmeric digested in potash is also used in dyeing skins red.

The fact will be noted that the native employs a mild acid

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similar to lime juice or the like to neutralize the ill effects of any excess of alkali. The yellow leather is stained by the juices extracted from a root known as "Gangammo." This root is said to be merely powdered up, mixed with water, and the mixture rubbed into the skin, which is then finished off as for red leather. It is possible that "Gangamma" may be finally identified botanically as turmeric; the sample submitted to the Imperial Institute resembled the poorer qualities of Indian turmeric. The African turmeric is the root stock of a species of *Canna*, having properties akin to the Indian turmeric of commerce.

Green leather seems to be a difficult color to produce with any degree of regularity, as the shades vary from a vivid green to bluish and even pale blue green. It has been suggested that these wide variations are produced by different combinations of indigo with the yellow dye materials. Mr. Gowers reports that in Bauchi, the green dye is made by mixing brass filings with a white salt named "Sunaderi," which is employed by the natives in brazing and welding metals. Milk and an infusion of tamarind fruit or lime juice are added to this mixture. After a time this mixture becomes green, a change which may be hastened by adding a quantity of a previous liquor. This concoction is rubbed over the grain until the skin is wet through to the flesh. When dried out, the deposit left on the grain side is carefully removed for future use. "Sunaderi" has been identified by the Imperial Institute as pure ammonium chloride, most probably imported.

The natives now appreciate the value and simplicity of the aniline colors, and it is to be feared that unless the administration grapple with the problem, as suggested earlier in this article, European materials and chemicals may be used to a much greater extent than they are at present, and thus alter time-honored methods of production to such a degree as to bring ruin on an invaluable export. The whole question is one of great economical importance to Nigeria's future.

The adminstration's line of action should be to direct the native how to make the best use of the materials at hand which have been tested by time, so that he may produce leather of the highest quality from the first-class Nigerian skins. This should not

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be a difficult matter provided the right man is obtained. If he acted cautiously, and did not introduce European methods, I see no reason why Niger leather should not sell for 50 to 100 per cent. above the price it commands to-day.

ABSTRACTS.

The Function of Enzyms. S. C. PRESCOTT, in *Science Conspectus*, Vol. 4, pp. 76-9, through *Chem. Eng.*, March, 1915. The transformation of materials in plant and animal organisms is effected by enzyms, which may be called the tools of cells, and the reagents by which the chemical reactions of the cell are produced. The term was suggested by the physiologist Kühne to designate the digestive ferments, such as pepsin, trypsin and ptyalin. The word has now been universally adopted to denote a group of chemical bodies, products of living cells, which effect the chemical operations of living matter, but which do not enter into the final products of these reactions. The number of enzyms is indefinitely large. A single micro-organism may produce several, and a human body many. It is not improbable that many enzyms are still unknown. There may be many intra-cellular enzyms, operating only inside the cell. Büchner's discovery of zymase and a method of preparing it in 1897 was the first great step in the study of intra-cellular enzyms, but little is known of them as yet. The chemical character of enzyms is not known. It has been assumed that they are protein-like. They may be regarded as a special and peculiar group of chemical compounds, differing in certain general ways from other substances. One of these differences is the great disproportion between the quantity of enzym and the amount of matter which it can change. Rennet can coagulate from 500,000 to 800,000 times its weight of casein without being used up. The activity of enzyms depends on the surrounding conditions of temperature, acidity, etc. Each enzym has its optimum temperature, just as each micro-organism has, and if heated beyond a certain temperature, its activity ceases, and the enzym itself is destroyed. They are also destroyed by poisons. Some enzyms require the presence of a special substance in order to act; others come from the cell in a condition independently active. Enzyms are classified with reference to the things on which they act, and form four general classes: oxidizing and reducing enzyms, splitting enzyms and hydrolyzing enzyms.

Iron Tannage ("Ferrox-Gerbung"). *Ledertechnische Rundschau.* The first iron-tanned leathers were very imperfect. Only a part of the iron absorbed by the hide was fixed, and the other portion of the metallic salts underwent gradual decomposition inside the leather, causing brittleness. The liquor for the "ferrox" tannage is prepared by forcing air through a solution of iron sulphate. Large quantities of iron are fixed to the fiber, and cannot be washed out. The leather is thoroughly washed

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after tanning, to remove the unfixed salts of iron. The resulting leather resembles vegetable tanned leather in color and general character. The cost of the process is very low, and the length of time required is only 2 or 3 days.

A Sensitive Torsion Balance. DR. FR. VOLLER. *Z. f. angew. Chem.*, Feb. 9, 1915. A horizontal spindle carries a light arm at right angles to the length of the spindle, a sector of copper and a spiral spring, the planes of the sector and spring being at right angles to the spindle. The spring is attached to the spindle at its center, the outer end being attached to a friction device, carrying a pointer and a handle by which it can be conveniently turned. The pointer swings in front of a circular scale. The article to be weighed is hung on a hook at the extremity of the arm first mentioned, drawing it down against a stop. The handle is now moved so as to cause the spring to lift the weight, until the arm comes opposite its zero point. The pointer now indicates on the scale the weight of the object in milligrams. The copper sector swings between the poles of a strong magnet, thus acting as a damper to check vibration. The instrument is made with a second scale, on which specific gravities may be directly read. For this work, a plummet adapted to the scale hangs in a vessel of the liquid whose specific gravity is desired. L. B.

Notes from the Tanning Courses at Pratt Institute. *Bulletin No. 26* of the Institute. On Friday, April 2, the annual tour of inspection began. The party numbered 25, including four instructors. The N. Y. Central provided a special car. The first stop was at Ashtabula, O., where the party inspected the plant of the Raser Tanning Co., manufacturers of automobile and furniture leather. The assistant superintendent of the plant, Alvin Swedenborg, is a graduate of the tanning course at Pratt. The party were the guests of the Raser Company at dinner, and afterward visited the greenhouses of Dunbar and Hopkins. Sunday was spent in Buffalo and at Niagara. On Monday, April 5, the plant of C. Moench & Sons Co., at Gowanda, N. Y., was visited. This tannery produces heavy chrome upper, vegetable leather and sole. Mr. Harmon Moench, superintendent of the beam-house and upper leather department, is a graduate of Pratt, and one of the first two men to specialize in leather at that Institute. The C. Moench & Sons Co. entertained the party at dinner, after which they visited the plant of the Eastern Tanners' Glue Co., and then were entertained by Mr. Harmon Moench at the Gowanda Club. On Tuesday, April 6, the sheep-skin tannery of Schoellkopf & Co., in Buffalo, was visited, as also the A. W. Hoppenstedt Laboratory. Here the party were shown around by A. W. Hoppenstedt, F. M. Loveland and Mr. Moore, the last named being a graduate of the tanning course at Pratt. The next place visited was the plant and laboratory of the Larkin Soap Co. On Wednesday, the 7th, the tannery of the Barnet Leather Co., at Little Falls, N. Y., was inspected. One of the gentlemen who acted as pilot was Mr. Laemmle, a graduate of the tanning courses at Pratt. After dinner, provided by the Barnet Co., the trip to Gloversville, via

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Fonda, was begun. Arrived at Gloversville at 4 P. M., the party put up at the Kingsborough, and next morning went to the factory of Fear & White, makers of glove leather and gloves. They were shown around by Messrs. F. V. Semple and F. W. Fear, both graduates of the tanning courses at Pratt. The next visit was to the glove factory of Louis Meyers & Sons. In the afternoon, the party went to the factory of the Donald Hayes Co., makers of buckskin leather and gloves, and afterward to the new factory of G. Levore & Co. On Friday, a visit was made to the plant of S. H. Shotwell & Son, manufacturers of mocha, ooze and suede leathers. By 6 P. M. the week's trip was completed by arrival at New York.

Cutch in Malaya. *J. Royal Society of Arts*, Mar. 26, 1915. In consequence of the serious shortage of tanning materials in England, the authorities of the Federated Malay States and the Straits Settlements have been making investigations with a view to directing the attention of British manufacturers to the possibilities of developing a trade in Malayan mangrove extract. In 1913 there passed through the ports of the Straits Settlements about 2,000 tons of mangrove cutch, valued at $150,000. Almost all of this came from Borneo. Half went to Germany, and one-fourth to Britain, the United States also getting a large slice, a little going to Spain and Denmark. The forest officials of these colonies report an area of 250 square miles of mangrove forests in the states of Pelak and Selangor. This is a government reserve and is worked for firewood only, the bark being a waste product. The Government is ready to encourage the establishment of extract plants in this region. Exports of mangrove cutch from North Borneo in 1913 amounted in value to $117,000.

Wattle-bark Supplies of British Colonies. *Commerce Reports.* The wattle-bark industry is of great importance in South Africa, particularly in Natal, and is rapidly increasing. The table shows the exports of wattle from the Union of South Africa, and the approximate average price per long ton of chopped bark in London from 1904 to 1913. The price at the end of October, 1914, was $37.72 per ton.

Years	Tons	Price per ton
1904	14,124	$46.84
1905	15,636	41.00
1906	14,828	43.80
1907	24,321	41.36
1908	24,849	39.54
1909	36,771	41.36
1910	41,344	39.54
1911	49,645	40.76
1912	52,776	35.28
1913	65,052	35.28

Shipments from Australia in 1911 and 1912 are shown in the table. Some bark other than wattle is included in these figures.

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	1911		1912	
	Tons	Value	Tons	Value
To Germany	7,424	$292,579	2,500	$100,396
Belgium	1,455	56,335	2,009	75,528
New Zealand	3,284	139,742	3,166	144,151
Other countries	455	17,319	217	8,535
Total	12,618	$505,975	7,892	$328,610

The chairman of the Wattle Growers' Association in British East Africa says that over 12,000 acres have been planted in that protectorate. During the next 2 years the annual output is expected to amount to 7,500 tons. The average tannin content of wattle bark is 32 per cent., thick bark being richer and of better color than thin. In Germany wattle (called by the Germans mimosa) has been chiefly used in the production of heavy leathers, but it furnishes a full, soft leather with calfskin and may well be used in making light leathers. Wattle leather has a faint reddish tinge, darkening slowly on exposure to light. A factory for the manufacture of solid wattle extract is being erected in South Africa.

Tannin for Holland: Tanning School. *Hide and Leather*, April 3. The direct shipment of tanning materials from the Dutch East Indies to Dutch ports is being substituted for importations through Hamburg and other German centers of distribution. In November, 1914, a new school of tanning was opened at Waalwyk, Holland. This is understood to be connected with the Government Experiment Station, and is under the direction of J. L. Van Gijn, well known to American leather chemists, and a member of the Association. The school is fully equipped with machinery, etc., and will give both practical and theoretical instruction.

Combination Tannage. W. EITNER. *Gerber*, Nos. 954, 956, 968, 970, 971. The purpose of combination tannages is either to produce a leather of certain definite properties which cannot be made by a single kind of tannage, or to imitate a leather made by a simple tannage by a combination method which is cheaper. In combination with vegetable tannage may be used chrome or aluminum salts, and certain salts of zinc; also artificial tanning materials such as neradol. Before considering the use of vegetable tannins at the same time with mineral salts, it is important to know what reactions take place between these substances. The salts of aluminum, sulphate, acetate and formate, and alum, have no effect on pure tannin, so that they may be used along with the latter. In the dyeing of silk, a mordant is used consisting of tannin and alum. Extracts containing tannin, as those of knoppern and sumac, have the less soluble portion of their tannin precipitated by aluminum salts, and the color of that which remains in solution is modified. Oil tannage may be used in combination with either vegetable or mineral tannage.

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For sole leather, combination of vegetable tannage with alum tannage was not to be considered, since alum tends to make a soft leather. Since chrome sole has been successfully made, the possibility of a combination of this method with vegetable tannage has been thought of. The earlier product of chrome sole lacked firmness and stiffness. By increasing the acidity of the liquors and so increasing their plumping power, the leather has been made better in these respects, although the speed of tannage is reduced. In spite of its great durability, chrome sole lacks some of the desirable qualities of vegetable tanned sole leather. The low yield is discouraging to the tanner, and this cannot be much improved by stuffing. The desirability of combining the good qualities of the two sorts has long been recognized. An article on the subject appeared in *Gerber*, No. 866 (Oct. 1, 1910). Hides for this purpose should be delimed and soaked and then agitated for 6 hours in a 15° liquor made from a decolorized extract. The liquor should be sweet and should not become sour during use. This preliminary tannage of the grain is very important, otherwise the acid chrome liquor, in consequence of its great swelling power, is liable to make a hard and brittle leather. The hides thus colored are rinsed and placed in the first chrome bath, which is quite acid. After 2 or 3 days the bath is strengthened, or the stock transferred to a second for 2 or 3 days more. A fresh chrome bath is prepared from 6 pounds of chrome alum or a corresponding quantity of other chrome salt for each 100 pounds of hide, together with 0.6 pound of sulphuric or 0.5 pound formic acid. These directions are suitable for heavy sole leather. For vache leather and sole resembling it, shorter treatment is sufficient, with half the quantity of acid. The tannage due to the two acid chrome baths is scant, but goes quite through the hide, and has an important influence on the following vegetable tannage. It prepares the hide to take up the tannin more readily by loosening the fiber bundles and so presenting a large surface for fixing the vegetable tanning material. Here also, in the third stage, a light tanning material, such as was used in the preliminary tannage, should be chosen. Cold soluble non-sulphited quebracho is very suitable, used in four handlers. The head handler may have a liquor of 25° barkometer, and the hides may remain 2 days in each. By this time they will be in a condition to be finished to good advantage by any of the familiar methods, either in the paddle with oak or pine bark, or with the heavier materials, myrobalans, valonia or knoppern or a mixture of such, or they may be finished in vats with extracts, or in a drum. In the second stage, instead of using only two chrome baths as described, these may be followed by others without addition of acid, made up from chrome alum or other chrome salts. This more intensive chrome treatment tends to increase the plumpness and yield of the leather, causing it to take up and firmly fix still more vegetable tannin, in contrast to sole leathers which are simply filled with extract, the greater part of which may be washed out. Leather prepared as above looks, both in color and other respects, somewhat unfamiliar. It is firm and full, and gives a

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high yield. In spite of its high tannin content it is not brittle, but remains tough. This last quality is one of the best results of the chrome treatment, which not only thoroughly tans the hide fibers, but by separating them permits much more rapid absorption of vegetable tannin. For the greatest gain of weight, it is best not to hurry the tannage in the later stages. In this case the saying "Time and tanning extract make weight" may fairly claim its place as a variant of the old adage "Bark and time make leather."

If in the second stage the hides are treated as above with two acid and two neutral chrome liquors, and also with two further chrome liquors made basic by the addition of soda, a fully tanned characteristic chrome leather is produced, which cannot be much changed by subsequent vegetable tannage, nor its weight much increased. (The translator questions the correctness of the last two statements.)

Thus far the use of other metallic salts instead of chrome for combination tannage has not been practiced in the production of sole leather, if we except a black sole leather made in Russia, in making which iron is employed, as it seems, more for the sake of the color than for tanning effect. Iron salts alone make a hard sole leather, which, however, shows so many faults that it is not serviceable.

Combination tannage for belting and harness leather is more satisfactory if aluminum or zinc salts are used instead of chrome, as they give a milder tannage than chrome. These combinations give a belting leather superior in tensile strength to straight vegetable tannage, but it is often inferior in appearance and yield. Hides intended for such tannage may be put through the same process outlined above for sole leather, as far as the chrome bath, instead of which is used a liquor made from alum, sulphate of alumina, sulphate of zinc or chloride of zinc, without the addition of acid or of salt. If zinc salts are used, they must be as free as possible from iron. Two liquors are used, the second (new) liquor being made up with 8 per cent. alum or zinc sulphate or 5 per cent. sulphate of alumina or 4 per cent. zinc chloride on the white weight. Although zinc sulphate has greater tanning power than alum, an equal quantity of it is used, since it tans more mildly and less rapidly. The zinc salts loosen the fiber bundles less than the aluminum salts, which makes zinc compounds well adapted for combination tannage of belting and harness and other leathers which need to have great tensile strength and resistance to stretching.

The hides stay 3 days in each liquor if aluminum compounds are used, or 4 days if the liquors are made with zinc salts, since the latter tan more slowly. The vegetable tannage following the use of alum or zinc salts can be completed in a relatively short time. Higher yields may be obtained if more than two mineral baths are used, the later ones being made basic by the addition of calcined soda. The best tensile strength and resistance to stretching are obtained, however, with the less heavily filled leather. After the mineral tannage, the hides are put through a series of from

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6 to 10 handlers, made up with gambier, oak or quebracho. The head handler in a series of 10 may have a strength of 25° barkometer, the hides being moved up each day. For a series of 6, the head may be 20°, and the hides remain 2 days in each liquor. The tail handler will be pretty well exhausted. After this treatment the hides will be found thoroughly tanned and of the greatest toughness. It is customary, however, to trim the hides to butts at this stage, and to drum the butts with extract, or lay them down for 12 to 14 days in a strong extract liquor. The latter process makes a leather which works better in the stuffing process than that filled by drumming. A still better product is made by laying away 4 or 6 weeks in a liquor of only 30° barkometer, of oak or decolorized chestnut or quebracho. Instead of laying away, drum tannage or a Vulcano tanning machine may be employed, with liquors of 30° to 50° barkometer. There was an old method of tannage for belting leather by means of a liquor of mixed mineral and vegetable tanning material. Hides unhaired with sulphide and cleaned are put into a series of handlers, in which 5 pounds of alum and 5 pounds of gambier (dissolved separately) are used for 100 pounds of white hide, added in portions during 5 days. The resulting leather, used for light belts, is called "orange leather." Instead of alum, zinc salts may be used.

Belt leather made by these methods has the character and appearance of vegetable leather, and it takes the place of the latter fully, possessing all the properties necessary for belt leather. For special purposes combination belt leathers are made in which the mineral tannage predominates, and which approach mineral-tanned leather in appearance. (Directions for stuffing belt leathers are given.)

The principal field for combination tannages has been and is in the making of upper leather. The oldest method used alum, salt and catechu together. The method now most used follows a preliminary chrome tannage with vegetable tannage. Both of these are employed in making kid leather. Kid tanned with alum finishes especially well if it has a subsequent treatment with gambier. Straight chrome kid, in order to take a good gloss in finishing, must be very fully tanned, which influences the toughness and wear unfavorably. A lightly chrome tanned kid, completed with gambier, has its toughness undiminished, and can be finished much more satisfactorily. Several combinations of alum, salt, flour, egg-yolk, oil and gambier are described. In those involving the use of egg-yolk, a third part of the egg-yolk may be replaced by a neutral water-soluble oil. Formulas are also given for combination tannage of sheep-skins, the resulting leathers being much used for the uppers of cheaper sorts of shoes. L. B.

Detection of Sulphite-Cellulose in Leather. W. MOELLER. *Collegium*' 1915, 99-101; *Rundschau,* Mar. 4. R. Lauffmann (abstract this J., Mar., 1915, p. 160 ff.) objects to Moeller's proposal to extract leather with cold, dilute caustic soda solution. Moeller believes Lauffmann's failure to

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obtain satisfactory results was due to too fine division of the leather. Appelius and Schmidt have also found that fine grinding of the leather is liable to make this reaction less distinct. Moeller has carried out a series of experiments and obtained results showing good agreement. The leather used had been tanned with liquors containing sulphite-cellulose both in the earlier and later stages, the whole process covering more than 3 months. It appears that the sulphite-cellulose by this long continued process becomes so firmly fixed to the hide as strongly to resist removal by either water or alkali. In such a case the extraction must be extended over a longer period in order to get a positive reaction. If the leather is coarsely divided, the quantity of hide substance going into solution in a given time is less than with a fine ground sample, so that on the addition of acid there is no heavy precipitate which would take up again the sulphite-cellulose which had gone into solution. As the author has pointed out before, the constituents of sulphite-cellulose extracts which are most absorbed by hide powder are most easily soluble in alcohol. In the case of mixtures of extracts, it is therefore advisable to treat the extracts with alcohol in order to separate the characteristic constituents of the sulphite-cellulose from as much as possible of the other substances present. The following form of Moeller's process is recommended: Instead of a cold, dilute water solution of caustic soda, a solution of 10 grams of caustic soda per 100 cc. absolute alcohol is used. Since hide substance is practically insoluble in hot alcohol, the extraction may be done with hot solution, and the time shortened materially. The leather extract is heated on the water-bath to drive off the alcohol, and the residue taken up in water, acidulated, filtered, and tested by the Procter-Hirst reaction. The author believes that this process will detect the presence of sulphite-cellulose in any leather containing it. He differs from Lauffmann (loc. cit.) in regard to the cause of the less strong reaction for sulphite-cellulose in older leather, holding that this is due to the more firm fixing of the sulphite-cellulose by hide fiber as time goes on, and that Lauffmann is not justified in supposing that the chemical properties of the sulphite-cellulose itself undergo change with time. L. B.

The Light-fastness of Anilin Colors, with Special Regard to the Colors Produced in the Leather Industry. ARTHUR BRÜHL. *Ledertechnische Rundschau,* No. 12, Mar. 25, 1915. Reprinting or abstracting this paper is forbidden.

PATENTS

Drying Varnished Leather. British Patent 20,795. A. GENTHE, Worms a. Rhein. Artificial light is used in a space kept as free as possible from vapor of water.

Combination Tannage. British Patent 16,844. W. A. KLIPSTEIN, New York. A mixture of quebracho extract, caustic soda, chrome sulphate and chrome oxide.

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CORRECTION.

In the May issue, in the report of the Committee on Comparative Analyses, page 234, Mr. F. M. Loveland is quoted as saying that he used S. & S. 590 paper in filtering non-tannins. The chairman of the committee, Mr. F. O. Sprague, asks that this be corrected to read "S. & S. 590 15 cm. paper for our soluble solids and 1F Swedish for non-tannins," the error having been made by the chairman in transcribing Mr. Loveland's report.

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FILTER PAPERS.

Committee Report, 1915.

By F. H. Small, Chairman.

The variable quality of S. & S. No. 590 filter paper has been the subject of criticism at the recent meetings of our Association. Our Secretary was instructed to seek through correspondence with the manufacturers a betterment of conditions, but his efforts,—judging by recent comments from members,—have met with only a small degree of success. Inasmuch as the above paper is the only one the use of which is permitted by our method for the determination of "Insolubles" any deficiencies in the paper are proper matters of grave concern. The one special merit of this paper is its low absorptive value, this being sufficiently low to be practically wholly nullified by the prescribed preliminary hour's digestion. Other papers tested from time to time have been so lacking in this merit as to make their substitution a matter of going from bad to worse. The need of an alternative paper at least as satisfactory for a filter as the No. 590 has been obvious and the difficulty, amounting to impossibility in some cases, of securing under present war conditions an adequate supply of the No. 590 has made the need urgent. To discover this alternative paper was in its essentials the task assigned the Chairman of this year's Committee on Filter Paper. There were some frills attached to the layout but these your Chairman detached.

On sounding out his Committee your Chairman found that with scarcely an exception the members had only one substitute paper to suggest and that was Swedish 1 F. This simplified matters amazingly and the work of the Committee resolved itself into a comparison of No. 590 and 1 F filter papers. Following is the letter of instructions sent the members and a tabulation of reports received.

> Under separate cover I am forwarding you samples for the work of the Committee on Filter Papers. These consist of a sample each of chestnut, oak bark, hemlock and quebracho extracts.
>
> No filter papers are included as one of the objects of the

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test is to ascertain the uniformity of papers as furnished by various chemical supply houses. The only paper at all generally recommended as a substitute for the S. & S. No. 590 is the Swedish I F and some of the members say regarding this latter that the cut papers are distinctly less uniform than the sheets. They recommend therefore that this be bought in sheets, which are then to be sorted—extra heavy and extra light being discarded—and the remainder cut for use. Your Chairman requests therefore that for your tests you use S. & S. No. 590 15 cm. filter paper from your regular laboratory supply; Swedish I F 15 cm. cut papers as supplied by the dealers; and Swedish I F 15 cm. diameter papers cut by you from sheets. In addition, test and report results on any other make of filter paper which you believe can be used as an alternative paper to the S. & S. No. 590.

The tests which you are requested to perform consist of a determination by the official method of the insolubles of each of the extracts with each kind of filter paper. You should so conduct your work as to eliminate as completely as possible all sources of variation other than the filter papers: for instance, prepare only one solution of each extract and use this for all the different kinds of papers; locate funnels containing the different kinds of papers as closely together as possible so as to have temperature and evaporation conditions as similar as possible, etc.

Do all work in duplicate and repeat the work on a second day. It is needless to add that the provisions of the method must be observed most strictly, the kaolin meet the requirements, etc.

Your report should include the following data: Total solids. Weights and percentages of all determinations.

For Each Kind of Paper.

Soluble solids, weights and percentages as above.
Time of collection of 100 cc. for evaporating.
Weight of each filter paper.
From whom paper was procured.
Character of filtrate.

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Oak Bark.

	Totals		Solubles									Insolubles						Diff. between papers
			Weight residues			Weight papers			Time of collection			590		1F cut		1F sheets		
	Per cent.	Diff.	590	1F cut	1F sheets	590	1F cut	1F sheets	590	1F cut	1F sheets	Per cent.	Diff.	Per cent.	Diff.	Per cent.	Diff.	
Alsop & McNutt . . 1	44.14		0.6454	0.6440	0.6475	0.8870	1.0540	0.9629	130	140	165	2.20		2.29		2.07		
2	44.08	0.06	0.6465	0.6451	0.6458	0.8875	1.0566	0.9636	130	165	135	2.13	0.07	2.22	0.07	2.19	0.12	
3	44.26		0.6536	0.6465	0.6510	0.9001	1.1460	1.0486	120	130	145	1.84		2.30		2.01		
4	44 29	0.03	0.6519	0.6485	0.6499	0.8128	0.9350	0.8896	120	150	130	1.95	0.11	2.17	0.13	2.08	0.07	
Av.	44.19	0 21	0.6493	0.6460	0.6486	0.8944	1.0479	0.9412	125	146	144	2 03	0.36	2.25	0.13	2.09	0.18	0.22
Helder 1	43.97		0.6520	0.6525	0.6516	1.0360	0.9711	1.0540	120	110	110	1.71		1.67		1.73		
2	44.01	0.04	0.6520	0.6525	0.6524	1.0393	0.9679	1.0580	110	110	120	1.71	0.00	1.67	0.00	1.68	0.05	
3	44.01		0.6480	0.6482	0.6490	1.0560	0.9490	1.0520	100	100	100	1.83		1.81		1.76		
4	43.94	0.07	0.6490	0.6480	0.6488	1.0574	0.9145	1.0330	100	100	100	1.76	0.07	1.83	0.02	1.77	0.01	
Av.	43.96	0.07	0.6502	0.6503	0.6504	1.0472	0.9506	1.0492	108	105	108	1.75	0.12	1.74	0.16	1.74	0.07	0.01
Oberfell & Richeson . 1	44.31		0.6528	0.6524	0.6523	0.919	0.8955	0.828	94	74	72	2.02		1.82		1.96		
2	44.31	0.00	0.6529	0.6537	0.6523	0.8975	0.8906	0.844	92	89	83	2.03	0.01	1.98	0.16	1.96	0.00	
3	44.29		0.6520	0.6527	0.6520	0.7993	1.013	0.966	120	95	95	2.08		2.05		2.11		
4	44.31	0.02	0.6517	0.6521	0.6517	0.9843	0.9532	0.8362	125	95	95	2.04	0.04	1.99	0.06	2.04	0.07	
Av.	44.31	0.02	0.6523	0.6527	0.6521	0.9000	0.9377	0.8685	103	88	88	2.04	0.06	1.96	0.23	2.02	0.15	0.08
Reed-Norris 1	44.24		0.6520	0.6530	0.6532	0.9341	0.8518	0.7750	169	136	101	1.92		1.86		1.84		
2	44.28	0.04	0.6524	0.6526	0.6534	0.9337	0.8172	0.8090	122	129	105	1.90	0.02	1.88	0.02	1.83	0.01	
3	44 34		0.6540	0.6540	0.6550	0.9052	0.8805	0.7870	98	96	106	1.87		1.87		1.81		
4	44.33	0.01	0.6542	0.6539	0.6550	0.9505	0.8380	0.6945	111	139	125	1.87	0.00	1.88	0.01	1.81	0.00	
Av.	44.29	0.10	0.6532	0.6534	0.6542	0.9309	0.8469	0.7664	100	125	109	1.89	0.05	1.87	0.02	1.82	0.03	0.07
Seltzer 1	44.30		0.6518	0.6474	0.6512	0.9495	0.9724	1.0540	144	349	158	1.98		2.26		2.02		
2			0.6516	0.6478	0.6487	0.9792	0.9414	1.0722	169	348	173	1.99	0.01	2.23	0.03	2.18	0.16	
3	44 38		0.6538	0.6486	0.6513	1.0311	0.9352	1.0141	206	301	191	1.93		2.25		2.09		
4			0.6524	0.6515	0.6530	1.0115	0.9312	0.9960	201	301	191	2.02	0.09	2.08	0.17	1.98	0.11	
Av.	44.34	0.08	0.6524	0.6488	0.6511	0.9928	0.9451	1.0341	180	325	178	1.98	0.09	2.21	0.18	2.07	0.20	0.23
Small & Miejnek . . 1	44.52		0.6558	0.6496	0.6516	0.995	1.030	0.910	120	165	108	2.19		2.59		2.46		
2	44.51	0.01	0.6530	0.6496	0.6502	0.965	1.070	0.900	108	155	120	2.25	0.06	2.47	0.12	2.44	0.02	
3	44.36		0.6529	0.6508	0.6501	0.9378	0.8993	0.9810	120	115	100	2.03		2.16		2.21		
4	44.28	0.08	0.6534	0.6513	0.6507	0.9636	0.8626	0.9169	154	120	115	2.02	0.01	2.16	0.00	2.20	0.01	
Av.	44.42	0.24	0.6538	0.6503	0.6506	0.9653	0.9655	0.9269	126	139	111	2.12	0.23	2.34	0.43	2.28	0.26	0.22
Smoot & Stacy . . . 1	44.28		0.6580	0.6580	0.6610	0.9396	1.0126	1.0662	230	137	158	2.05		2.05		1.85		
2	44.37	0.09	0.6572	0.6584	0.6578	0.9462	0.9860	1.0792	180	160	117	2.10	0.05	2.02	0.03	2.06	0.21	
3	44.44		0.6598	0.6586	0.6586	0.9572	1.0994	1.0148	246	205	140	2.03		2.10		2.11		
4	44.40	0.04	0.6620	0.6586	0.6606	0.9678	1.0766	1.0154	230	180	134	1.85	0.18	2.10	0.00	1.98	0.13	
Av	44.37	0.16	0.6592	0.6584	0.6595	0.9527	1.0437	1.0439	222	171	137	2.01	0.25	2.07	0.08	2.00	0.26	0.07
Wisdom 1	44.41		0.6576	0.6575	0.6573	0.913	0.950	0.983	143	118	162	1.71		1.71		1.73		
2	44.41	0.00	0.6578	0.6572	0.6577	0.860	1.000	0.829	164	128	147	1.70	0.01	1.73	0.02	1.71	0.02	
3	44.51		0.6567	0.6568	0.6565	0.845	1.028	0.895	159	133	161	1.87		1.86		1.86		
4	44.51	0.00	0.6565	9.6562	0.6568	0.900	0.966	0.875	172	132	197	1.88	0.01	1.90	0.04	1.86	0.02	
Av.	44.46	0.10	0.6571	0.6569	0.6571	0.879	0.986	0.985	159	128	167	1.79	0.18	1.80	0.19	1.79	0.17	0.01
Yocum & Faust . . . 1	44.09		0.6438	0.6469	0.6474	0.8149	0.9152	0.9152	265	220	220	2.35		2.15		2.12		
2	44.16	0.07	0.6477	0.6501	0.6547	0.8659	0.9894	0.9890	290	265	265	2.37	0.02	2.22	0.07	1.92	0.20	
3	44.30		0.6525	0.6544	0.6506	0.8650	0.8678	1.0067	310	171	245	2.09		:.96		2.21		
4	44.34	0.04	0.6504	0.6472	0.6492	0.8957	0.7522	0.9975	227	227	310	2.14	0.05	2.35	0.39	2.22	0.01	
Av.	44.22	0.25	0.6486	0.6496	0.6505	0.8604	0.8811	0.9771	273	221	260	2.24	0.28	2.17	0.39	2.12	0.30	0.12
Gen. Av.	44.28	0.13	0.6529	0.6518	0.6527	0.9358	0.9560	0.9447	155	161	145	1.98	0.18	2.04	0.20	1.99	0.18	0.11

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	Totals		Solubles									Insolubles						Diff. between papers
			Weight residues			Weight papers			Time of collection			590		1F cut		1F sheet		
	Per cent.	Diff.	590	1F cut	1F sheet	590	1F cut	1F sheet	590	1F cut	1F sheet	Per cent.	Diff.	Per cent.	Diff.	Per cent.	Diff.	
Alsop & McNutt . . 1	91.16		0 4593	0.4589	0.4608	0.8672	1.0540	0.9865	120	120	120	10.57		10.64		10.33		
2	91.14	0.02	0.4599	0.4589	0.4619	0.8672	1.0542	0.9690	120	120	120	10.47	0.10	10.64	0.00	10.13	0.20	
3	91.29		0.4654	0.4635	0.4611	1.0587	1.1883	1.0672	135	120	120	9.61		9.95		10.37		
4	91.23	0.06	0.4714	0.4666	0.4632	0.7970	0.8400	0.8225	135	120	120	8.56	1.05	9.40	0.55	10.00	0.37	
Av.	91.21	0.15	0.4640	0.4620	0.4618	0.8975	1.0391	0.9613	128	120	120	9.80	2.01	10.16	1.24	10.21	0.37	0.41
Helder 1	91.22		0.4708	0.4703	0.4710	1.0451	0.9310	1.0250	75	64	64	8.69		8.78		8.66		
2	91.33	0.11	0 4705	0.4709	0.4716	1.0320	0.9450	1.0430	75	64	64	8.74	0.05	8.67	0.11	8.55	0.11	
3	91.04		0.4705	0.4700	0.4690	1.0207	0.9702	1.0234	60	60	60	8.54		8.63		8.80		
4	91.09	0.05	0.4693	0.4700	0.4690	1.0100	0.9541	1.0280	60	60	60	8.75	0.21	8.63	0.00	8.80	0.00	
Av.	91.17	0.29	0.4703	0.4703	0.4702	1.0270	0.9501	1.0299	68	62	62	8.68	0.21	8.68	0.15	8.70	0.25	0.02
Oberfell & Richeson . 1	90.75		0.4667	0.4683	0.4675	0.9218	0.8775	0.8240	63	63	63	8.89		8.56		8.66		
2	90.66	0.09	0.4686	0.4655	0.4678	0.8295	0.9912	0.8295	63	63	63	8.49	0.40	9.10	0.54	8.72	0.06	
3	90.74		0.4672	0.4664	0.4668	0.8710	1.032	0.9077	72	72	67	8.73		8.85		8.79		
4	90.55	0.19	0.4669	0.4657	0.4658	0.9523	1.067	0.8428	72	72	67	8.79	0.06	8.99	0.14	8.99	0.20	
Av.	90.68	0.19	0.4674	0.4665	0.4670	0.8937	0.9919	0.8510	68	68	65	8.73	0.40	8.88	0.54	8.79	0.33	0.15
Reed-Norris 1	91.14		0.4673	0.4657	0.4660	0.9178	0.8385	0.7455	120	113	100	9.11		9.39		9.34		
2	91.04	0.10	0.4665	0.4661	0.4660	0 9200	0.8602	0.6960	113	105	95	9.27	0.16	9.32	0.07	9.34	0.00	
3	91.23		0.4677	0.4674	0.4670	0.9661	0.8683	0.8255	101	96	96	9.22		9.27		9.34		
4	91.30	0.07	0 4681	0 4670	0 4668	0.9397	0.7890	0.8212	99	101	94	9.15	0.07	9.34	0.07	9.37	0.03	
Av.	91.18	0.26	0.4674	0.4666	0.4665	0.9359	0.8390	0.7721	108	104	96	9.19	0.16	9.33	0.12	9.35	0.03	0.16
Seltzer 1	91.70		0.4641	0.4648	0.4650	1.0400	0.9640	1.0482	154	120	94	10.28		10.15		10.12		
2			0.4648	0.4653	0.4647	1.0562	0.9690	1.0854	144	120	94	10.15	0.13	10.07	0.08	10.17	0.07	
3	91.62		0.4656	0.4644	0.4652	1.0200	0.9499	0.9500	125	125	115	9.94		10.15		10.00		
4			0.4662	0.4658	0.4654	1.0138	0.9550	0.9499	155	130	120	9.81	0.13	9.90	0.25	9.97	0.03	
Av.	91.66	0.08	0.4652	0.4651	0.4651	1.0325	0.9595	1.0084	145	124	106	10.05	0.47	10.07	0.25	10.07	0.20	0.02
Small & Mlejnek . . 1	91.55		0.4704	0.4674	0.4670	1.015	0.960	0.890	60	76	60	8.84		9.37		9.43		
2	91.60	0.05	0.4671	0.4660	0.4649	0.966	1.045	0.945	76	60	76	9.23	0.39	9.23	0.14	9.81	0.38	
3	91.53		0.4673	0.4652	0.4640	0.907	0.870	0.962	70	60	60	8.93		9.30		9.52		
4	91.24	0.29	0.4708	0.4690	0.4675	0.967	0.899	0.943	76	60	60	9.00	0.07	9.32	0.02	9.59	0.07	
Av.	91.48	0.36	0.4689	0.4669	0.4659	0.966	0.944	0.935	71	64	64	9.00	0.39	9.31	0.14	9.59	0.38	0.59
Smoot & Stacy . . . 1	91.00		0.4684	0.4652	0.4694	0.9346	0.9950	1.0248	115	150	105	9.28		9.82		9.09		
2	91.20	0.20	0.4664	0 4656	0.4688	0.9168	1.0000	1.0260	145	140	105	9.62	0.34	9.76	0.06	9.20	0.11	
3	90.88		0.4675	0.4675	0.4684	1 0716	1.0522	1.0246	132	150	110	9.10		9.10		8.94		
4	90 68	0.20	0.4665	0.4645	0.4688	1.0944	1.0600	1.0270	130	154	114	9.28	0.18	9.62	0.52	8.88	0.06	
Av.	90.93	0.52	0.4672	0.4657	0.4689	1.0044	1.0268	1.0256	131	149	109	9.32	0.52	9.58	0.72	9.03	0.32	0.55
Wisdon 1	90.72		0.4707	0.4693	0.4688	0.928	1.065	0.947	104	104	128	8.17		8.42		8.50		
2	90.77	0.05	0.4709	0.4700	0.4686	0.857	1.060	0.949	105	97	113	8.14	0.03	8.29	0.13	8.54	0.04	
3	90.88		0.4701	0.4688	0.4683	0.900	0.943	0.824	132	87	108	8.36		8.59		8.68		
4	90.79	0.09	0.4702	0.4688	0.4685	0.871	0.995	0.895	122	87	105	8.34	0.02	8.59	0.00	8.64	0.04	
Av	90.79	0.16	0.4705	0.4692	0.4686	0.889	1.016	0.904	116	94	114	8.25	0.20	8.47	0.30	8.59	0.18	0.34
Yocum & Faust . . . 1	91.04		0.4634	0.4622	0.4652	0.8635	0.8175	0.9143	140	140	140	9.62		9.83		9.31		
2	90.79	0.25	0.4640	0.4669	0.4666	0.8530	0.8514	1.0557	140	140	140	9.52	0.10	9.01	0.82	9.06	0.25	
3	91.42		0.4684	0.4685	0.4703	0.8963	0.9635	0.9299	170	129	100	9.37		9.37		9.04		
4	91.68	0.26	0.4675	0.4685	0.4701	0.8868	0.9125	0.8699	169	205	100	9.53	0.16	9.37	0.00	9.08	0.04	
Av.	91.23	0.89	0.4658	0.4665	0.4681	0.8749	0.8862	0.9425	155	154	120	9.51	0.25	9.40	0.82	9.12	0.27	0.39
Gen. Av.	91.15	0.32	0.4674	0.4665	0.4669	0.9467	0.9614	0.9366	110	104	95	9.17	0.51	9.32	0.47	9.27	0.26	0.29

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		Totals		Solubles									Insolubles						Diff. between papers
				Weight residues			Weight papers			Time of collection			590		1F cut		1F sheets		
		Per cent.	Diff.	590	1F cut	1F sheets	590	1F cut	1F sheets	590	1F cut	1F sheets	Per cent	Diff.	Per cent.	Diff.	Per cent	Diff.	
Alsop & McNutt	1	36.84		0.5805	0.5772	0.5807	0.8794	1.0595	0.9600	53	53	53	0.38		0.38		0.37		
	2	36.94	0.10	0.5797	0.5781	0.5798	0.8901	1.0545	0.9570	53	53	53	0.43	0.05	0.53	0.05	0.42	0.05	
	3	36.89		0.5817	0.5780	0.5808	0.9802	1.1298	1.0450	50	50	50	0.32		0.55		0.35		
	4	36.90	0.01	0.5799	0.5795	0.5793	0.8228	0.9400	0.9067	50	50	50	0.42	0.10	0 45	0.10	0.47	0.12	
	Av.	36.89	0.10	0.5805	0.5782	0.5802	0.8931	1.0459	0.9672	52	52	52	0.39	0.11	0.53	0.13	0.40	0.12	0.14
Helder	1	37.04		0.5870	0.5870	0.5870	1.0490	0.9040	1.0330	37	29	29	0.23		0.23		0.23		
	2	37.05	0.01	0.5870	0.5870	0.5870	1.0466	0.9600	1.0380	29	29	29	0.23	0.00	0.23	0.00	0.23	0.00	
	3	36.96		0.5830	0.5830	0.5830	1.0490	0.9339	1.0147	26	26	26	0.23		0.30		0.30		
	4	36.91	0.05	0.5840	0.5830	0.5830	1.0220	0.9474	1.0170	26	26	26	0.23	0.00	0.30	0.00	0.30	0.00	
	Av.	36.99	0.14	0.5855	0.5850	0.5850	1.0417	0.9514	1 0257	30	28	28	0.23	0.00	0.27	0.07	0.27	0.07	0.04
Oberfell & Richeson	1	36.81		0.5818	0.5814	0.5813	0 8475	0.9825	0.952	28	28	28	0.23		0.25		0.25		
	2	36.83	0.02	0.5821	0.5817	0.5818	0.835	1.016	0.936	28	28	28	0.25	0.02	0.27	0.02	0.27	0.02	
	3	36.75		0.5802	0.5796	0.5805	0.986	0.9959	0.9706	27	27	27	0.27		0.24		0.23		
	4	36.78	0 03	0.5809	0.5812	0.5813	0.8693	0.963	0.8167	27	27	27	0.29	0.02	0.32	0.08	0.27	0.04	
	Av.	36.79	0.05	0.5812	0.5810	0.5812	0.8909	0.9894	0.9188	28	28	28	0.26	0.06	0.27	0.08	0.26	0.04	0.01
Reed-Norris	1	36.86		0.5838	0.5840	0 5830	0.8997	0.7947	0.7820	36	33	37	0.14		0.13		0.19		
	2	36.86	0.00	0.5836	0.5834	0.5830	0.9425	0.8380	0.8537	29	35	31	0.16	0.02	0.16	0.03	0.19	0.00	
	3	36.92		0.5849	0.5844	0.5843	0.9645	0.8724	0.7551	30	29	26	0.14		0.17		0.18		
	4	36.94	0.02	0.5849	0.5840	0.5843	1.0117	0.8523	0.6847	32	29	27	0.14	0.00	0.20	0.03	0.18	0.00	
	Av	36.89	0.08	0.5843	0.5839	0.5837	0.9546	0.8394	0.7689	32	32	28	0.14	0.02	0.17	0.07	0.19	0.01	0.05
Seltzer	1	36.95		0.5835	0.5832	0.5830	0.9856	0.9770	1.0123	40	37	34	0.25		0.27		0.24		
	2			0.5834	0.5835	0.5833	1.0239	0.9416	1.0006	40	37	32	0.20	0.05	0.25	0.02	0.26	0.02	
	3	37.04		0.5862	0.5852	0.5853	0.9868	0.9243	1.0230	38	40	30	0.17		0.24		0.23		
	4			0.5852	0.5864	0.5861	0.9980	0.9540	1.0602	38	40	30	0.24	0 07	0.16	0.08	0.18	0.05	
	Av.	37.00	0.09	0.5846	0.5846	0.5846	0.9998	0.9492	1.0240	39	39	32	0.22	0.08	0.23	0.11	0.23	0.08	0.01
Small & Mlejnek	1	37.07		0.5867	0 5844	0.5844	0.995	0.940	0.945	24	32	24	0.20		0.35		0.35		
	2	36.83	0.24	0.5834	0 5835	0.5814	1.005	1.015	0.965	24	32	24	0.32	0.12	0.32	0.03	0.45	0.10	
	3	36.99		0.5870	0.5865	0.5871	0.9712	0.8994	0.9060	28	34	28	0.23		0.26		0.22		
	4	36.90	0.06	0.5830	0.5828	0 5825	0.9914	0.8545	1.0130	28	34	28	0.25	0.02	0.27	0.01	0.28	0.06	
	Av.	36.94	0.24	0.5850	0.5843	0.5838	0 9907	0.9275	0.9572	26	33	26	0.25	0.12	0.30	0.09	0.33	0.23	0.08
Smoot & Stacy	1	36.85		0.5864	0.5900	0.5886	0.9594	0.9760	0.8716	26	23	23	0.04		0.04		0.13		
	2	36.97	0.12	0.5880	0.5904	0.5876	0.9180	0.9740	0.8550	24	27	18	0.04	0.00	0.01	0.03	0.19	0.06	
	3	36.83		0.5900	0.5858	0.5882	1.0272	1.0528	0.9534	29	38	21	0.20		0.24		0.09		
	4	36.87	0.04	0.5900	0.5882	0.5872	1.0210	1.0827	0.9972	28	27	21	0.10	0.10	0.09	0.15	0.15	0.06	
	Av.	36.86	0.14	0.5887	0.5887	0.5879	0.9814	1.0214	0.9193	27	29	21	0.10	0.16	0.10	0.23	0.14	0.10	0.04
Wisdom	1	36.90		0.5837	0.5842	0.5858	0.865	1.093	1.042	46	40	41	0.12		0.17		0.07		
	2	36.92	0.02	0.5835	0.5842	0.5856	0.871	1.045	0.748	40	40	35	0.14	0.02	0.17	0.00	0.08	0.01	
	3	36.93		0.5937	0.5847	0.5846	0.824	0.975	0.881	39	31	42	0.21		0.15		0.16		
	4	36.91	0.02	0.5835	1.5845	0.5844	0.875	1.018	0.801	42	36	38	0.23	0.02	0.16	0.01	0.17	0.01	
	Av.	36.92	0.03	0.5836	0.5844.	0.5851	0.859	1.033	0.868	42	37	39	0.18	0.09	0.16	0.02	0.12	0.10	0.06
Yocum & Faust	1	36.72		0.5889	0.5885	0.5922	0.8474	0.8153	1.0567	65	65	65	0.32		0.35		0.12		
	2	36.76	0.04	0.5884	0.5870	0.5853	0.8482	0.8217	1.0700	60	60	65	0.17	0.15	0.26	0.09	0.36	0.24	
	3	36.95		0.5856	0.5851	0.5867	0.8133	0.7962	0.9343	60	40	40	0.35		0.39		0.29		
	4	37.06	0.11	0.5819	0.5823	0.5823	0.8718	0.8840	1.1176	55	45	55	0.43	0.08	0.40	0.01	0.40	0.11	
	Av.	36.87	0.34	0.5862	0.5857	0.5866	0.8452	0.8293	1.0446	60	53	56	0.32	0.26	0.35	0.14	0.29	0.28	0.06
Gen. Av		36.91	0.14	0.5843	0.5839	0.5842	0.9102	0.9540	0.9427	37	37	34	0.23	0.09	0.26	0.10	0.25	0.11	0.05

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	Totals		Solubles: Weight residues			Solubles: Weight papers			Solubles: Time of collection			Insolubles: 590		Insolubles: 1F cut		Insolubles: 1F sheets		Diff. between papers
	Per cent.	Diff.	590	1F cut	1F sheets	590	1F cut	1F sheets	590	1F cut	1F sheets	Per cent.	Diff.	Per cent.	Diff.	Per cent.	Diff.	
Alsop & McNutt . . 1	43.43		0.6020	0.5982	0.6019	0.8948	1 0499	0.9642	175	150	150	3.54		3.80		3.55		
2	43.38	0.05	0 6027	0.5990	0.6000	0 8950	1.0490	0.9650	135	150	150	3.50	0.04	3.74	0.06	3.68	0.13	
3	43.21		0 6000	0.5987	0.5992	1.0274	1.1860	1.0525	150	160	130	3.46		3.54		3.51		
4	43.16	0.05	0.5970	0.5986	0.6013	0.7977	0.9005	0.8634	160	130	145	3.66	0.20	3.55	0.01	3.35	0.16	
Av	43.29	0.27	0.6004	0.5986	0.6006	0.9037	1.0688	0.9363	155	147	144	3.54	0.20	3.66	0.26	3.52	0.33	0.14
Helder 1	43.49		0.6110	0.6145	0.6113	1.0396	0.9400	1.0533	100	95	95	3.04		2.81		3.03		
2	43.49	0.00	0.6120	0.6135	0.6116	1.0303	0.9300	1.0570	90	95	90	2.98	0.06	2.88	0.07	3.01	0.02	
3	43.47		0.6110	0.6109	0.6110	1.0284	0.9460	1.0170	105	105	105	3.02		3.02		3.02		
4	43.40	0.07	0.6105	0.6105	0 6110	1.0240	0.9461	1.0138	120	120	105	2.98	0.04	2.98	0.04	2.95	0.07	
Av	43.46	0.09	0.6111	0.6123	0.6112	1.0328	0.9405	1.0352	104	104	99	3 00	0.06	2.92	0.21	3.00	0.06	0.08
Oberfell & Richeson . 1	43.36		0 6053	0.6039	0.6065	0.896	0.9405	0.8730	125	110	125	3.31		3.38		3.53		
2	43.39	0.03	0.6051	0.6041	0.6040	0 835	0.9805	0.909	117	125	110	3.31	0.00	3.38	0.00	3.41	0.12	
3	43 28		0.6001	0.6039	0 6035	0.8621	1.0048	0.976	105	105	125	3.36		3.50		3.20		
4	43.35	0.07	0 6057	0.6057	0.6053	0.9574	1.0034	0.9174	120	105	105	3.38	0.02	3.38	0.12	3.38	0 18	
Av.	43.34	0.11	0.6050	0.6044	0.6049	0.8876	0.9823	0.9188	117	106	111	3.34	0.07	3.41	0.12	3.38	0.33	0.07
Reed-Norris 1	43.45		0.6065	0.6053	0.6080	0.9778	0.8045	0.7655	123	142	104	3.29		3.36		3.19		
2	43.45	0 00	0.6067	0 6055	0.6078	0.9033	0.8720	0.8425	120	124	113	3.27	0.02	3.35	0.01	3.20	0.01	
3	43.62		0.6070	0.6055	0.6060	1.0124	0.8820	0.8511	163	136	137	3.41		3.51		3.28		
4	43.50	0.03	0.6060	0.6058	0.6088	0.9076	0.8388	0 8640	163	155	116	3.44	0.03	3.49	0.02	3.29	0.01	
Av	43.53	0.17	0.6007	0.6055	0.6080	0.9728	0 8493	0.8308	142	139	115	3.35	0.17	3.43	0.16	3.24	0.10	0.19
Seltzer 1	43.42		0.6037	0.6012	0.6018	1.0069	0.9203	1.0331	140	240	174	3.44		3.61		3.57		
2			0.6024	0.6007	0.6005	1.0000	0.9409	1.0749	165	244	169	3.53	0.09	3.64	0.03	3.65	0.08	
3	43.59		0.6037	0.6017	0.6030	1.0248	0.9471	1.0652	219	264	204	3.61		3.74		3.66		
4			0.6049	0.6023	0.6019	1.0150	0.9466	1.0843	219	259	204	3.53	0.08	3.70	0.04	3.73	0.07	
Av.	43.51	0.17	0.6037	0.6015	0.6018	1.0124	0 9402	1.0644	186	252	188	3.53	0.17	3.67	0.13	3.65	0.16	0.14
Small & Mlejnek . . 1	43.78		0.6066	0.6065	0.6053	0.995	0.985	0.910	108	120	108	3.53		3.53		3.59		
2	43.71	0.07	0.6060	0.6040	0.6039	0.950	1.015	0.905	120	120	108	3.60	0.07	3.77	0.23	3.78	0.19	
3	43.54		0.6007	0.6072	0 6050	0.9529	0.9031	0.9856	120	140	100	3.27		3.47		3.45		
4	43.44	0.10	0.6060	0.6058	0 6068	0 9502	0.8645	0.9860	115	135	115	3 45	0.18	3.30	0.17	3.35	0.10	
Av.	43.62	0.34	0.6065	0.6050	0.6052	0.9620	0 9419	0.9486	116	129	108	3 46	0.33	3.52	0.47	3.54	0.43	0.06
Smoot & Stacy . . . 1	43.60		0.6054	0.6030	0.6060	0.9490	0.9680	0.8658	174	205	120	3.19		3.35		3.15		
2	43.49	0.11	0.6070	0.6034	0.6050	0.9520	0.9424	0.9000	157	177	168	3.09	0.10	3.33	0.02	3.18	0.03	
3	43.62		0.6038	0.5986	0.6042	1.0678	0.9218	0.9110	153	126	148	3.34		3.68		3.31		
4	43.56	0.06	0.6038	0.6060	0.5980	1.0560	1.0130	1.0584	165	155	138	3.34	0.00	3.19	0.49	3.68	0.37	
Av	43.57	0.13	0.6050	0.6049	0.6038	1.0062	0.9613	0.9338	162	167	143	3.24	0.25	3.39	0.49	3.33	0.53	0 15
Wisdom 1	43.60		0.6118	0.6105	0.6114	0.888	0.948	0.990	174	133	167	3 06		3.15		3.09		
2	43.56	0.04	0.6118	0.6112	0.6119	0.925	1 076	0.916	197	133	162	3.06	0.00	3.10	0.05	3.11	0.02	
3	43.57		0.6066	0.6080	0.6080	0.803	1.091	0 825	174	151	180	3.21		3.32		3.32		
4	43.50	0 02	0.6090	0.6086	0.6078	0 855	1.007	0.851	174	132	196	3 21	0.00	3.38	0.06	3.33	0.01	
Av.	43.58	0.04	0.6105	0 6096	0.6095	0.883	1.030	0 896	179	139	176	3.13	0.15	3.24	0.28	3.21	0.24	0.11
Yocum & Faust . . . 1	43.27		0.5982	0.6033	0.6008	0.8212	0.8454	1.0942	235	190	190	3.49		3.21		3.38		
2	43.32	0.05	0.6047	0.6002	0.6092	0.8148	0.8952	0.8717	225	225	190	3.36	0.13	3.26	0.05	3.06	0.32	
3	43.43		0.6070	0.6063	0.6063	0.8098	0.8561	1.0925	200	200	200	3.37		3.41		3.41		
4	43.48	0.05	0.6254	0.6270	0.6264	0.8864	0.7874	1.1179	215	200	200	3.31	0.06	3.36	0.05	3.43	0.02	
Av.	43.38	0.21	0.6098	0.6108	0 6107	0.8480	0.8460	1.0441	219	204	195	3.38	0.18	3.31	0.15	3.32	0.37	0.07
Gen. Av.	43.47	0.17	0.6066	0.6057	0.6062	0.9434	0.9511	0.9564	153	154	142	3.33	0.17	3.39	0.25	3.35	0.28	0.11

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Total volume of soluble solids filtrate collected from which 100 cc. was evaporated.

Range of temperature of room and of solutions during test.

In addition kindly answer the following questions:

Were your funnels and collection glasses covered during the preliminary digestion?

What is your opinion of the merits of the several papers tested?

What percentage of each sort of paper would you expect to reject for defects, over- or under-weight, etc.?

What recommendations have you to make as a result of your work?"

Comparing the general averages we find that so far as this work shows there is little difference in the speed of filtration of the several papers, the 1 F sheet showing perhaps a tendency to filter a trifle the most rapidly.

All the papers give filtrates of satisfactory clearness and no one seems to excel in this particular. One man complains that the 1 F cut papers are "unquestionably different from the 1 F sheets and fail to return absolutely clear filtrates in the case of the quebracho extract;" another remarks that the 1 F papers give "higher insoluble percentages due to more efficient filtration."

As to uniformity of weight the general opinion is that there is little choice. The comparatively wide weight variations of the No. 590 are too well known to need comment, but the 1 F either cut or sheet seems to be equally bad in this particular. The following table offered by Alsop and the weights shown in the tables above are sufficient evidence.

The question arises, however, whether excessive fussiness in this particular is warranted. Faust in his comments remarks, "I found a very large difference in the weights of the papers cut from these sheets (1 F). However, this difference in weight does not seem to have any appreciable effect on the results found." Reed and Norris write "We would call attention to the fact that the weight of the filter paper seems to have but little influence upon the resulting soluble solids as shown by our figures, although it is very possibly true that excessively heavy papers would have

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COMPARATIVE WEIGHTS OF FILTER PAPERS.

	No. 590 S. & S. Grams	No. 1F cut Grams	No. 1F sheets Grams.	How sheets were cut
*1	0.8404	*0.9450	0.9310	
2	0.9550	1.0450	0.9883	
3	0.9656	1.0419	0.9807	
4	1.0274	1.0499	0.8634	
5	0.9185	1.0490	0.9940	
6	1.0587	1.0150	1.0380	
7	0.9311	1.0578	0.8225	
8	0.9561	1.0905	0.9905	
9	0.9405	1.0924	0.9905	
10	0.8431	1.0124	0.9905	
11	0.8380	1.0466	0.9935	
12	0.8280	0.8400	0.9685	
13	0.8495	1.0610	0.9600	
14	0.8311	1.0715	0.9813	
15	0.8827	1.1860	0.9715	
16	0.7977	1.1460	0.9850	
17	0.8948	1.1174	0.9629	
18	0.8498	1.1043	0.9213	
19	0.7970	1.0595	0.9870	
20	0.8672	1.0545	0.9840	
21	0.8672	1.0540	0.9690	
22	0.8519	1.0542	0.9982	
23	0.9099	1.0328	0.9482	
24	0.8250	1.0600	0.9223	
25	0.8877	1.0900	0.9496	
26	0.9127	0.9612	0.9344	
27	0.8829	1.1037	0.8896	
28	0.8598	1.0665	1.0235	
29	0.9012	1.1132	0.9642	
30	0.8950	1.0340	0.9306	
31	0.8311	1.0137	1.0305	
32	0.8794	1.0635	0.9269	
33	0.8875	1.0232	0.9067	
34	0.8228	1.0950	1.0089	
35	0.8228	1.0672	0.9650	
36	0.8128	1.0050	0.9075	
37	0.8678	1.1200	1.0525	
38	0.8628	1.1243	1.0391	
39	0.8482	1.0011	0.9636	
40	0.9075	0.9775	1.0082	
41	0.8250	0.9350	1.0377	
42	0.9004	0.9005	0.9827	
43	0.9200	0.9400	0.9990	
44	0.9802	1.1883	0.9570	
45	0.8901	1.1210	0.9370	
46	0.9901	1.0750	1.0486	
47	0.9678	1.0679	1.0673	
48	0.9596	1.0994	0.9910	
49	0.9652	1.1298	0.9970	
50	0.9550	1.0740	1.0450	

1	4	7
2	5	8
3	6	9

10	13	16
11	14	17
12	15	18

19	22	25
20	23	26
21	24	27

28	31	34
29	32	35
30	33	36

37	40	43
38	41	44
39	42	45

* First 50 papers from full package of filter papers.

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a noticeable influence." So far as this investigation discloses the weight of the filter paper used has no effect on the insolubles percentage found. A study of the tables will show no relation between weight of filter paper and weight of soluble solids residue. This is not saying that such relation may not exist, but that in the present state of the method such relation if it does exist is completely masked by other factors and at present we should worry more about these other factors than about varying weights of filter papers.

It is perhaps after all varying texture rather than varying weight that has bothered us in the 590 paper and this largely as it has caused excessive breakage in pleating. From the viewpoint of economy,—eliminating from consideration any rejects for varying weight,—the use of 1 F filter paper is certainly advantageous. Its first cost is less; practically all the collaborators agree that it shows fewer pin holes and can be pleated with a much smaller percentage of loss from breakage.

In the essential point of uniformity of filtration no one of the papers shows any superiority so far as evidenced by the figures in the table.

For each extract the average insolubles figure yielded by each kind of paper differs from that yielded by the others by an amount well within the limit of experimental error.

It seems apparent, therefore, that we may permit the use of 1 F paper either cut or in sheets without danger of altering the soluble solids figure as found under the requirements of our present method. The net result of this investigation would seem to be a demonstration that variations in analytical results due to the use of 590 or of 1 F filter papers, or to papers of either kind, of weights varying within the limits used in this investigation are negligible as compared with existent variations due to other causes.

Just what these other causes are, what variations in manipulations, laboratory conditions, personal factor, etc., affect most markedly the ultimate result your Chairman has no means of determining. He would call attention to a few points that suggest themselves.

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Five collaborators cover funnels and dishes during preliminary digestion; two, funnels alone; and two neither.

Some collaborators collect a definite amount of soluble solids filtrate, 110 or 120 cc. from which to pipette, others amounts varying from 101 to 130 cc. Just how the man who collects only 101 cc. manages to do his pipetting is rather a mystery to the Chairman. A rather large assortment of pipettes would seem necessary if a dry pipette is used for each solution while a shift without rinsing from a solution of 0.45 gram to the 100 to one of 0.65 gram to the 100 does not seem conducive to accuracy.

When one collaborator collects his soluble solids filtrate for pipetting in 60 minutes while another requires 170, or one in 100 while another requires 300 it would imply rather pronounced differences of manipulation. Various explanations are possible,—differences of pleating whereby more or less filtration surface is presented to the liquor; variation in throwing the kaolin on the paper whereby the pores of the paper are more or less completely clogged; varying degrees of fineness of the kaolin; varying degrees of fineness of the insolubles precipitate in the flask.

Temperature conditions, even under our present regulations undoubtedly play a prominent part in determining the percentage of insolubles found. For instance, Alsop writes, "On the first day the temperature of the room in which the solutions were allowed to cool over night was practically 20°. It became colder and the solutions for the next day were put in a warmer place. As is not unusual here the weather changed again before morning and in consequence the solutions were 29° and had to be cooled to 20° in water. This sort of thing is a 'condition and not a theory' and does make a difference sometimes with some materials."

As to some of these matters we may effect improvements; variations due to some are possibly negligible. However, notwithstanding all these possible causes of variations, the Chairman believes it is safe to say that the figures in the table show on the whole a rather satisfactory concordance.

The Chairman would recommend that line 1 of section 10 of the "Official Method for the analysis of vegetable materials containing tannin" be altered to read that—"S. & S. No. 590 or Munktells 1 F 15 cm. single, pleated, filter paper shall, etc."

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A QUICK METHOD OF TANNING.*

By H. R. Procter.

The present difficulty with regard to tanning materials and the desirability of the quick production of leather recall to my mind an experiment which I made a quarter of a century ago, but have never seriously followed up. Butts were taken from the handlers only just struck through, and after draining for a short time in pile were laid flesh upwards and thickly coated with a mixture of strong hemlock extract liquor and the fine powder of divi-divi. The mixture was quite pasty, and laid on to the thickness of ⅜ or ½ inch. The goods were then placed flesh to flesh and made into piles of perhaps 20 butts, a layer of the divi-divi chaff, which contained but little tannin, being placed between each pair so as to separate the grains, and they were allowed to lie for a time which I forget precisely, but which might extend to a day or two. After this, if my memory serves me, they were simply put down in a strong liquor and allowed a short layer, possibly not more than a day or two, and were then washed free of the divi-divi paste, finishing with a clean liquor—probably myrobalans—and shedded in the usual way. The color was good and very little redder than usual, the hemlock extract having scarcely reached the grain, and was so compact and firm that the customer to whom I sold them was anxious that I should supply more of the same tannage. I think my reason for not pursuing the matter further was my fear of the goods heating in pile, as the weather was warm, but this danger could be greatly minimized by the addition of carbolic acid or some other effective antiseptic to the paste. The theory of the process was that the layer of dry divi-divi chaff absorbed the exhausted liquor from the butts, the place of which was taken by the very concentrated tanning solution of the paste. Mangrove, or any other cheap extract—even if dark-colored—could be substituted for the hemlock, and finely ground dry bark for the divi-divi chaff. The divi-divi was simply passed through a disintegrator and screened, the finer powder being practically a very rich solid extract. Of course, algarobilla could be used in the same way. It would, of course, be a wise pre-

* Letter to the *Leather Trades Review*, April 28.

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caution not to allow the liquors containing divi to mix with the general layer liquors of the yard, but to work them rapidly away through the suspenders. If any tanner cares to experiment upon these lines, I should be much interested in hearing confidentially or otherwise the result of his experiments.

TREATMENT OF INDUSTRIAL WASTES.*

By Langdon Pearse.[1]

The treatment of industrial wastes is a problem that is fast becoming of great importance not only to the manufacturer, but also to the municipal corporation. Industrial wastes may not only increase the likelihood of nuisance in a stream through the presence of putrescible organic matter, but may also add to the load on a treatment plant or materially alter the conditions to be met in a prospective plant.

From the standpoint of keeping streams clean, the control of wastes is important in order to avoid deposits as well as unsightly appearance caused by floating material or oily scum. Again, from the standpoint of drinking water certain wastes are unpleasant, as for instance where the discharge from pertoleum refineries may produce a noticeable kerosene taste in the water supply taken from a neighboring intake. Other wastes are deleterious from the standpoint of fish life, for some contain ingredients which are highly injurious. In particular, the refuse from gas and tar works is troublesome, even in small amounts, as it may taint the flesh of fish with a tarry taste, and render them wholly unfit for food.

From the standpoint of the manufacturer, the forced treatment of industrial wastes has sometimes proved profitable, as happened in the paper industry at a time when fine save-alls were not in common use. The introduction of fine screens in pulp mills saved daily many tons of finely divided pulp. In the packing industry in the early days, blood and other refuse was thrown away and the handling of this, partly by persons seeking profit

* *S. & L. Rep.*, April 22, 1915. pp. 49-53.

[1] Division Engineer, in charge Sewage Disposal Investigation, the Sanitary District of Chicago.

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and partly to avoid nuisance, has produced a considerable source of revenue. On the other hand, under the competitive stress of operation the loss of valuable material to the sewers has been often reduced to a comparatively small percentage. Consequently additional treatment to remove the percentage remaining may prove expensive. As a general rule it is not safe offhand to assume that a direct profit can be made from the treatment of industrial wastes. But in general an indirect return is received by removing the cause, and subsequent cost of litigation, and thereby reducing the charges resulting from lack of attention to modern sanitary standards.

With the growing demands in most large cities for cleanliness and the higher standards set by the different authorities both federal and state, and the increased number of authorities whose wishes have to be met, the average manufacturer looks askance upon the sanitary engineer, and considers him as one more load to be carried, and consequently a source of annoyance rather than profit. Likewise the sanitary engineer frequently finds that the material troublesome to a stream from the standpoint of sewage purification is in such shape that it is difficult to treat, and is largely waste which the manufacturer desires to be rid of at the smallest expense.

Utilization of By-Products.—In some industries, in the small plants, the economies of the large plant in facilities for making by-products are lacking. However, careful inspection by an outsider of engineering training will frequently show leaks which can be stopped at small expense with comparative profit to the manufacturer. In the tanning industry, pieces of skin and even whole hides have been lost to the sewer by lack of proper floor screens and catch basins. In one wool scouring plant so much wool went down the sewer that the owners refused their operating engineer the privilege of keeping the catch basin clean for the wool recovered.

In the location of new plants, a manufacturer should bear carefully in mind the almost certain probability of regulation of the discharge of waste. Hence it would seem wisdom to locate plants producing large amounts of waste difficult of treatment on the largest bodies of running water available. Unfortunately,

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in many cases this is not done, and a plant is built on a stream which furnishes hardly enough water for an adequate water supply. And then all but the sanitary engineer are astonished when a nuisance results.

Classification of Wastes.—From the physical and chemical standpoint, the various wastes can be classified as follows:

1. Wastes carrying sediment or suspended matter.
   - *a.* Heavy mineral matter, such as marble dust, ashes, etc., usually inert.
   - *b.* Heavy matter, such as the product of chemical reactions as tarry waste from gas works, residues from ammonia works, etc.
   - *c.* Heavy organic matter—which may be highly putrescible, or comparatively inert.
2. Wastes carrying little or no sediment.
   - *a.* Containing soluble organic matter, which may be highly putrescible.
   - *b.* Containing chemicals.
     1. Eager to absorb oxygen.
     2. Inhibiting bacterial action.
3. Wastes carrying both suspended and soluble matter.
4. Wastes carrying floating materials.
   - *a.* Volatile and inflammable, as for instance gasoline or kerosene.
   - *b.* Fats and oils.
   - *c.* Light organic matter.
   - *d.* Light matter the product of chemical reaction as floating material from gas wastes, etc.

These classifications are of service to indicate simply the general types of material which may be present. The wastes to be handled vary considerably with the industry, and even among plants of the same industry, according to the processes used and the material produced. The prevalent waste differs in the various states. In Indiana, for instance, strawboard wastes are very common, whereas in Ohio, creamery and wire mill waste occur, in Maine, the pulp and sulphite waste, and in Illinois, the wastes from the packing houses, tanneries, starch works and distilleries

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are most common. At times canneries give trouble. These are usually found near the argicultural districts.

Sources and Amount of Waste.—In studying an industry from the standpoint of treatment of the waste, the first essential is to learn the processes carried on, and the probable sources and amounts of waste. Seldom does the manufacturer know just how much sewage he is discharging. A thorough inspection of the plant in all its details is of value, for frequently the study of the inside workings reveals many points at which waste can be reduced with comparatively small expenditure of material and labor. No general method of procedure can be stated, as each plant is usually a law unto itself. At times, separation of the wastes may be desirable, whereas in other cases, as for instance in tannery work, the effluent from another part of the plant contains chemicals that may be of material value in precipitating material held in suspension in the effluent from another part of the plant. Under those conditions, mixing of the wastes is of service. Rain water and surface water drains generally should be kept out of the sewer systems receiving waste in order to avoid at times of rain serious overloading and scouring out of the material which should be retained.

Methods of Treatment.—The methods of treatment available are somewhat more varied than for domestic sewage, although for the most part the same general principles apply. The difficulty is, of course, to find the proper constants and loading which can be used to produce results. Owing to the diversity of practice in many plants, the sure way is to try out what can be done with the individual case in question. With wastes containing no suspended matter, ample dilution frequently suffices Sometimes this dilution can be furnished artificially from storage reservoirs. Again it is available in large streams such as the Mississippi or other rivers with sufficient flow. Where the dilution is not adequate, and velocities are low, the suspended matter in wastes containing such must be reduced in order to avoid deposits in the stream. Screening and sedimentation are available for this purpose. Screening seems eminently suitable for the coarser wastes, such as come from the stockyards, slaughterhouses, beet sugar works, pulp mills, etc., where material slow

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to digest can be readily removed by a fine mesh screen. The disposal of the screenings when putrescible may, however, be complicated with the problem of avoiding nuisance. Sometimes the material can be dried and burnt. Occasionally it can be turned back into the processes. Directly comparative results available in the packing industry would indicate that considerable material is left over after fine screening, which can be removed by settling. However, the screening removes much which is slow to settle and is a source of scum in sedimentation tanks.

Systems of Settling.—Settling should remove practically all the suspended matter, the actual per cent. depending on the waste, the period of settling, the type of tank, and the velocities used. A double-deck tank is frequently most suitable where much scum producing material is present. In extreme cases, fine screening has been proposed as a preliminary treatment to reduce the scum forming material. With comparatively inert material, the Dortmund type of tank with sloping bottom may prove successful if properly and frequently cleaned. On tannery waste, particularly from the limes, heavy material is present which will quickly settle. In wool pulleries or wool scouring shops, much heavy grit is produced which also drops quickly. For such gritty waste a grit chamber readily cleansible, is desirable. Unfortunately, many of the tanks now in operation in tanneries and elsewhere are expensive to clean, as the entire work has to be done by hand on days when the plant is shut down.

Chemical Precipitation.—Chemical precipitation may materially increase the removal of suspended matter by settling, and in some rare cases may be produced by the combination of chemicals already in solution in wastes from the various processes in the plant, particularly in tanneries.

Septic tanks were once widely used in the past, and are used occasionally to-day, despite their limitations, on creamery, canning and tannery wastes where organic matter slow to decompose needs breaking down. As a rule, however, the septic tank is not regarded favorably on account of liability of nuisance and the larger storage required to hold liquid for many days. Very frequently further treatment is required to produce an effluent needing but slight if any dilution.

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In Massachusetts, intermittent sand filters have been used freely in experimental work, as well as in actual practice, but of late sprinkling filters have been found helpful, particularly as a preliminary to intermittent sand filtration, in connection with tannery or other wastes high in organic matter, thereby permitting much higher rates of application to the sand filters. In Chicago, on the mixed waste from Packingtown, a sprinkling filter has proved adaptable in handling mixed stock-yards and domestic sewage thoroughly settled. Owing to the possibility of deposits of grease in such a filter, its history is being watched over several years.

Evaporation.—Occasionally a waste is so difficult to handle and contains so much material in solution that evaporation appears to be the only remedy. Although the economy of evaporation is markedly increased by the use of several effects, the process is expensive, particularly for dilute wastes. It has, however, proved practicable in the packing industry for evaporating "tank" water from the rendering tanks which contains matter of value as a fertilizer, and has also been applied in evaporating distillery wastes, as well as in recovering chemicals from industrial processes where they can be used over again to advantage and profit.

Sludge Problems.—As in the treatment of domestic sewage, a sludge problem soon looms up for the quantity of sludge found in industrial waste is frequently much greater than in domestic sewage. The amount varies widely. In the mixed waste tested at the Center Avenue station of the sanitary district, the amount of sludge in an Emscher tank was approximately 10 cubic yards per million gallons, as compared with about 1 cubic yard found at 39th Street, on domestic sewage. In the tannery tanks with plain sedimentation from 10 to 100 cubic yards per million gallons are found. However, in the tannery industry the flows are not usually great, so that the total volume of sludge produced in a day is not quite so appalling as the figures might indicate although large enough.

The treatment of the sludge depends largely on the waste itself. Where there is a large mass of material to be disposed of with little value except for filling, the expense is for trans-

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portation to the nearest dump. Frequently with proper treatment on organic wastes, a quick drying sludge may be produced, as for instance by the use of the double-deck type of tank on the mixed packing house waste. Such sludge may contain some nitrogen, but it is not commonly regarded at present as a valuable material. Sludge pressing may reduce the water content. Under certain conditions, the sludge itself may prove of value for the recovery of fat, and once the fat is extracted, the dried sludge may serve as a filler for fertilizer. The basic value as a fertilizer from the laboratory standpoint, may be doubtful on account of what the chemists call the difficulty of the assimilation of the nitrogen by the soil. A sure test is the actual trial of the sludge in the field.

Estimating Strength of Waste.—In testing the strength of industrial waste the sanitary engineer is primarily interested in the oxygen demand, particularly where the stream flow available is limited. This can best be determined by the use of a dilution test or the nitrate test devised by Dr. Lederer. The comparison of strength of sewage by this method is of value, and is impressive even to the layman. In the sanitary district, the domestic sewage at 39th Street has been found to have a bio-chemical oxygen demand averaging 100 to 125 p. p. m., with a consumption of approximately 25 to 30 per cent. in the first 24 hours at 20° C. The mixed stock-yards and packing house wastes average 900 to 1,300 p. p. m., with a consumption of about 20 per cent. in the first 24 hours.

Tannery Waste.—Tannery wastes vary considerably, ranging from 400 to 1,000 p. p. m., with consumption averaging around 7 per cent. in the first 24 hours. The consumption in the first 24 hours at 20° C. has a direct bearing on the condition to be met in a stream if 24 hours is the interval of time to the critical point. Other time periods may be taken for study, if desired, to meet local conditions.

Plants to Handle Waste.—In the design of works to handle industrial waste, the manufacturer is usually anxious to cut the cost of installation to a minimum, and consequently the most careful designing is required. Where a plant is located in a city in the midst of a built-up region, lack of space is a great handi-

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cap. Although willing to employ legal talent the manufacturer is frequently averse to engaging competent engineering advice. Consequently it sometimes happens that more funds are frittered away in ill-considered experiments that would produce a practical working plant of service, and this phase is occasionally complicated by the eager salesman who urges devices which from their very principle could be ruled out as impractical or insufficient from the start.

Self-Cleansing Sewers.—Inside any industrial plant, self-cleansing sewers are a necessity, with plenty of manholes for ready inspection. In the tanning industry, provisions should be made on the floors at all inlets to the sewers to hold back large pieces of material, such as skin and the like, by suitable screens of perforated plates set in the floor over the outlet drains. Some of the most up-to-date factories are equipped with catch basins under every inlet. The exact efficiency of this is, however, unknown. On lines of sewer, the use of fine screens may be desirable to separate out material that is hard to handle and material which might interfere with the proper working of pumps or other machinery.

Cleaning Settling Tanks.—Settling tanks should be designed for ready cleaning, as hand cleaning is expensive, although still practiced in most tanneries. The experience in the Chicago district would indicate that a tank with bottom slopes over 45 and near 30° from the vertical will feed the sludge to the center of the tank. However, the sludge may become so caked, if cleaning is infrequent, as to be difficult to pump. Compressed air, water or steam introduced at the bottom of the tank just before pumping will break up the sludge and render it easily handled. Wood, leather strips, or other foreign material which will tend to clog a small centrifugal should be screened out. Ample sludge drying beds and sludge storage should be provided.

Skimming Basins.—Skimming basins are also useful to hold back grease, or light oils. Grease may occur either in a form which tends to float, or to be held in suspension, or to sink. In hot liquids, basins of large surface area are used. These are the reverse of settling basins, in that scum retaining baffles are provided with scant sludge retaining features. Among these are

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found the skimming basins built to catch oils from the locomotive shops or round houses, as well as to catch tar and refuse escaping through the sewers from gas works, and works for the utilization of tar and gas works waste. In many cities there are now municipal requirements in force which require traps to retain gasoline and oils escaping from garages. In Chicago a triple basin is used suitably trapped and baffled for this purpose.

Methods of Sewage Treatment.—The sanitary engineer to-day realizes that sewage can be treated either by aerobic or anaerobic methods to arrive eventually at the same stage, the breaking down and transformation of putrescible organic matter. The anaerobic methods attack organic matter vigorously, but are difficult to control and liable to produce serious nuisance. Consequently, the sanitary engineer has endeavored in the treatment of domestic sewage to keep the sewage as fresh as possible throughout the sewers and treatment. In the height of the septic tank vogue, the anaerobic decomposition applied too generously disgusted many manufacturers, and proved to their minds at least, from the foul liquids and odors produced, that their wastes were incapable of any treatment. However, other methods available to-day of screening, settling, and aerobic treatment should be tried before final opinion is pronounced. It is rather curious that the septic tank should have been discovered in England and there patented, when for years the Chicago River and Bubbly Creek had been operating as a septic tank, probably the largest in the world, yet censured by all who passed by. Consequently, with Bubbly Creek as an example, it is now difficult to see why the same method was followed in the hope of securing results free from nuisance. In any sewage treatment, either industrial or domestic, the greatest possible freedom from odors is desirable, as well as absence of ill-smelling liquors. Here the suspended matter should be removed as quickly as possible. There may, however, be some wastes in which the use of septic processes is still of service.

Municipal Officials.—In approaching the manufacturer from the standpoint of the sanitary official of a municipality, it is unwise to arouse any false hopes as to the possibility of recovering values from the wastes, although in some few instances treatment of industrial wastes has been profitable. As a rule the manu-

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facturer feels that little escapes to the sewers of value to him, and promptly forgets that much may escape which is troublesome to the sanitarian, particularly he who is charged with carrying out the sanitary regulations and laws necessitated by the concentration in the cities and the growth of populations draining into streams.

The municipality has a basic interest in the wastes discharged by industries, even though the domestic sewage be not treated, from the standpoint of sewer maintenance. Consequently, in most cities, ordinances will be found regulating the methods of entrance to the sewers, and prescribing catch basins and other devices suitable to retain settling material which may cause deposits. Oil is also undesirable. Gasoline and other volatile fluids should rigorously be kept out of the sewers. The intelligent interpretation of these ordinances by an engineer familiar with industrial processes and the application of engineering principles, materially helps in holding back a great deal of material at its source and by so doing relieves expensive maintenance of the sewers. Recently in another city, paunch manure from packing houses completely stopped a 24-inch outfall sewer for a distance of 120 feet, flooding the adjoining back-yards. This necessitated the removal and rebuilding of the sewer.

Separate Treatment of Waste.—The question of treatment and whether it is best to treat industrial wastes separately or mixed with domestic sewage is a problem which must be solved for each case. However, the principle seems clear that many wastes which are difficult of treatment alone can be more readily handled when diluted with domestic sewage. In this classification, particularly, are wastes which are sterile at their source and which by dilution with domestic sewage are thoroughly seeded with bacterial life required for self-purification. Wastes slightly acid may be neutralized by the alkalinity of the sewage and seeded thereby. The problem is largely one of economy and expediency for each locality. Occasionally hints can be gained by comparison of methods employed in different industries. For instance, in the mining field a great deal has been accomplished on special devices for the classification and concentration of fine slimes to secure economy in cost and operation. To some other industries these same devices may be applicable.

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Unless there is a degree of nuisance existing and law-suits threatened or underway, it is difficult to interest the manufacturer in remedial measures, although a spirit of co-operation is growing which meets conditions and suggests remedies before conditions become acute. The manufacturer is already burdened with minute inspections by Federal officials for articles used in interstate commerce, and city ordinances are also enforced, covering smoke, odors, etc. Consequently, when the sanitary authorities step in and ask treatment of sewage, scant heed is paid to their desires. Hence, many remedial works have been built largely to avoid or settle lawsuits, and not as a study for profit.

The Burden of Cost.—The point of great interest to the manufacturer is, who will bear the burden of cost. The laws in various countries differ. In England, for many years during the early history of sewage disposal, the industry was favored, some of the local regulations even going so far as to permit the manufacturer to discharge freely into a stream when he could prove to the satisfaction of the courts that it was impossible to treat his wastes in a practical manner, but of late the practice has been swinging the other way, and the manufacturer is asked to bear a large part if not the whole share of the cost. In the United States there is no settled practice, the requirements of every state varying. Sometimes the city has borne part of the burden, requiring the industry to make its sewage at least as good as the domestic sewage. Again the entire burden is placed on the industry. In some extreme cases the industry has been required to remove its sewage from the city sewers and treat it separately. Very largely each case has been handled on its merits with diverse results. On navigable streams the Federal statutes are explicit, with the result that there appears to be ample precedent for forcing the industry depositing settling matter to remedy the conditions. Undoubtedly with the extended scope of the Public Health Service the pollution of the interstate streams by industries will be regulated in a more uniform fashion throughout the country.

Co-operation with Health Officials.—The health official, as well as the sanitary engineer, is interested in accomplishing results. As a rule, the best results can be obtained by co-operation based on a thorough knowledge of the facts in each particular case and a

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careful, conservative study and trial of the applications of known principles of sanitary engineering. With the confidence of a manufacturer secured in this manner; a great deal can be accomplished and far more of value secured than by the collection of fines from time to time for the infraction of rules and the neglect of adequate remedial measures.

THE ADULTERATION OF LEATHER.*

By J. A. S. Morrison, M. Sc.

Recent criticism of the leather used in army boots has led me to the conclusion that few shoemakers recognize the extent to which adulteration is practiced nowadays. The majority of trade writers seem to be surprised that so much bad leather has been put into boots, but, to an analytical chemist constantly engaged in the examination of sole leathers, the wonder is that Government buyers have not been sufficiently warned by those experts who have been called into consultation. It is safe to say that almost 50 per cent. of the bottom stuff offered by responsible firms is in some way adulterated. I am led to classify adulteration of leathers under two headings: (1) Gross adulteration; (2) adulteration carried out scientifically, so that an analyst will in some cases be led to pass the leather.

The following will show examples of grossly adulterated leathers:

TABLE I.

Description	Epsom salt Per cent.	Glucose Per cent.	Barium salts, as barytes Per cent.
Ro. hide bellies	4.0	8.1	—
Belly fleshes	6.4	—	—
Ro. hide bellies	4.8	5.24	—
Australian bellies	nil	6.1	—
Ro. hide bellies	nil	4.77	—
Canadian bends	nil	10.2	—
Ro. hide bellies	8.6	—	—
Canadian bends	nil	4.8	—
Ro. hide bellies	—	—	3.8
Ro. hide bellies[1]	—	—	—
Lifting bellies	5.8	2.8	—

[1] 4 per cent. of silicious matter.

* *Leather World*, Mar. 11, 1915.

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An examination of the figures in this table will show that these leathers have been wilfully adulterated—that is to say, the method of addition must have been carefully thought out, the adulterants must have been added as such, and the ability of the leather to hold such adulterant must have been determined by experiment. Such adulteration cannot be defended, but one must recognize that the shoe manufacturer, in the majority of cases, gets what he pays for. Then, too, the manufacturer who has a costing system worth the name must eventually find that such leather does not pay to cut up. This method of adulteration, whilst to be condemned, has the saving grace that it is adulteration pure and simple.

Turning to my second classification, I would draw attention to the following results.

TABLE II.

Description	Epsom salt Per cent.	Glucose Per cent.	Barium salts, as barytes Per cent.
Belly fleshes	3.23	3.5	—
Belly fleshes	1.13	1.0	—
Ro. hide bellies	2.70	3.50	—
Ro. hide bellies	nil	2.63	—
Belly fleshes	2.7	—	1.0
Ro. hide bellies	1.98	2.61	—
American bends	nil	2.6	—
Ro. hide bellies	nil	3.2	—
Sole bend	nil	3.8	—
Sole bend	—	2.6	—
Ro. hide bellies	1.3	—	—

An examination of the above results will show that (1) the glucose content is such that it approximates to the I. A. L. T. C. limit; (2) the mineral ash of the added mineral adulterant will generally be such that the total ash falls below the I. A. L. T. C. limit of 2 per cent.

One is bound to say that this form of adulteration is clever, and that it generally achieves its object. Indeed, one is reminded of the practices of the margarine makers who set out to make butter substitutes which just passed analytical requirements. Few shoe manufacturers engage the services of an analytical chemist for systematic investigation of their purchases, the only check for the majority being in the costing department. It will

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thus be admitted that the possibility of finding adulteration by this method is only certain when adulteration is heavy, and that when leather is adulterated to the extent of 2 to 3 per cent. it is generally passed. Nor can we wonder that it is passed when we consider that consignments from the same yard will often vary 2 to 3 per cent. in moisture content. This leads me to the charge that many tanners are carrying out this adulteration knowing full well what they are doing, and are, in addition, giving a spurious guarantee that their leather is not adulterated.

It is the general custom of the writer, when he finds a leather falling under the above class, to ask the tanner for a guarantee. The stereotyped reply is that the tanner "guarantees the leather free from barium salts." He states, in addition, "that no Epsom salt or glucose is used in his yard," but "that so many extracts are heavily adulterated with these substances that it is not possible to guarantee that his leather is entirely free from them. If such be present, the quantities must be very small indeed." This reply is not an isolated one; I have received it from many tanners, of whom one at least has a well-equipped chemical laboratory, and must know what is purchased in the form of extract. Then, too, if tanners take the trouble to get extract free from barium salts, why do they not carry their vigilance further and make sure that extracts do not contain Epsom salt and glucose?

I am strengthened in my criticism by the following incident which came to my notice a short time ago. In a northern city a currier, ostensibly in a small way of business, failed for a considerable amount. A committee of inspection was formed, and found that the debtor had been buying the finest chestnut extract; with it he mixed large amounts of glucose and Epsom salt, and then offered the new product as a finishing extract. This extract was bought by some of the largest firms in the trade, who were owing money at the time, and who paid up very quickly when requested to do so. The sole cause of the failure was the flight of a foreign partner with a great part of the spoils. Were it not for this gentleman's flight the business would still have been flourishing, for great profits were being made. These facts were vouched for by a member of the committee of inspection. My contention is that the blending of these extracts is carried

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out solely with the object of producing leather which will just pass the I. A. L. T. C. limits.

The I. A. L. T. C. may say that these matters do not come within the scope of its labors, but I feel that, with a little firmness on its part, much may be done to stop such sharp practices. It has often been stated that some leathers may contain 3 per cent. of glucose solely derived from the tanning materials used. Granted that this may be so, how many of the modern tannages contain even 1 per cent. of glucose derived from the tanning materials used? In my experience, the majority of modern tannages produce a leather containing less than 1 per cent. of glucose, and this being so, the present limit is evidently only retained in order that no harm be done in exceptional cases.

UTILIZATION OF CÆSALPINIA DIGYNA.*

Cæsalpinia digyna is a thorny, scandent shrub, found plentifully in a wild state in many parts of Burma and in Bengal and Assam. It occurs chiefly on level ground, especially on waste land near villages and in hedgerows, where the soil is of a sandy character. The plant avoids land which is saturated during the rains.

When fully grown the shrub reaches a height of about 10 feet. The leaves are similar to those of the tamarind, but the pod is smaller, from 1¼ to 2 inches long, and from ⅔ to ¾ inch wide, with thick margins. Each pod contains as a rule two nearly black pea-like seeds, between which the pod is constricted.

The value of cæsalpinia digyna ("Ţeri") pods as a tanning material appears to have been discovered first in the year 1847. A short account of the experiments carried out at that period is given in the *Indian Agricultural Ledger* for 1899, No. 9. The question of the commercial utilization of the pods appears, however, to have been left in abeyance for many years.

In 1893 the officiating reporter on economic products at Calcutta instituted an inquiry into the matter, and arranged for the submission of three samples to the Imperial Institute for examination. A report which was furnished to the authorities in India

* *Bulletin* of the Imperial Institute, through *Leather Trades Review*, April 14, 1915.

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on the results of this investigation is quoted in the *Agricultural Ledger* referred to above, and also in *Technical Reports and Scientific Papers* (Part I, p. 192), published by the Imperial Institute in 1903. Two further samples were forwarded to the Imperial Institute in 1900, and the results of their examination are also given in the latter volume, p. 193. A sixth sample was examined at the Imperial Institute in 1903.

The results of the examination at the Imperial Institute of the various samples are as follows (the analytical figures refer to the pod-cases freed from the seeds):

RESULTS OF ANALYSIS.

Sample	Place of origin	Moisture in material as received Per cent.	Tannin in dried material Per cent.	Total soluble matter in dried material Per cent.	Ash Per cent.
1	Burma	11.07	53.82	69.7	2.28
2	Burma	10.93	53.86	70.4	3.76
3	Assam	11.4	59.89	74.2	1.84
4	Assam	13.72	45.45	64.4	2.30
5	Burma	13.17	59.5	82.6	2.10
6	Burma	10.8	54.5	73.0	2.78

From the above results it is clear that the pod cases of cæsalpinia digyna contain a high percentage of tannin. Technical trials which were arranged for by the Imperial Institute showed that the material was suitable for use by European tanners, and inquiries which were received after the publication of the first report indicated that there would be a good market for the pod cases if they could be exported from India in large and regular quantities.

Under these circumstances the Indian authorities were asked to ascertain the quantity of cæsalpinia digyna pods available for export. As a result of numerous inquiries instituted by the Forest Department the following estimates, which relate to the whole pods including the seeds, were obtained.

1. The Officiating Conservator of Forests at Maymyo, Burma, reported that it was estimated that some 10,000 pounds of cæsalpinia digyna pods could be delivered by rail at Rangoon at Rs.11 per 100 pounds, *i.e.*, about Rs.240 (£16) per ton, and a further 6,000 pounds or more could probably be delivered by river steamer at a similar price.

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2. The Divisional Forest Officer in the Minbu division of Burma estimated that about 40,000 pounds of the pods could be placed on the market at Rs.75 (£5) per ton.

It will be seen that the above estimates are widely different. The inquiries indicated that the wild pods could only be collected in small quantities and at an excessive cost, and that consequently an export trade could only be established by cultivating the plant on a large scale.

A small quantity of about 600 pounds of the whole pods was collected in 1908 by the Deputy Conservator of Forests at Pyinmana, Burma, and a sample was forwarded to the Imperial Institute. The sample was submitted to an English firm of tanners, who had expressed interest in cæsalpinia digyna, and they offered to purchase the total quantity at the rate of £18 per ton in London. This was eventually agreed to by the Indian authorities, who, however, stated that the whole pods could not be profitably exported at less than £22 per ton in London. The latter price, however, included a Government royalty of about £8 per ton.

The firm found the pods to be of excellent quality, and stated that if the price were reasonable they were prepared to buy up to as much as 5 tons weekly. They added that the commercial use of the pods would depend upon their price as compared with such materials as quebracho, myrobalans and sumac.

Quite recently an experimental consignment of the whole pods was sold in London at £14 per ton.

The experimental cultivation of cæsalpinia digyna has been suggested by the Imperial Institute to the Indian authorities on various occasions, and the attention of Indian planters was called to the commercial value of the pods by a notice inserted in the *Indian Trade Journal* for 1910, p. 356. It is, therefore, possible that in the future regular supplies of the pods may be available for export.

As practically all the tannin is contained in the pod cases or husks it would be necessary to separate the seeds, and export the husks only. In some trials made on a small scale at the Imperial Institute it was ascertained that the centrifugal palm nut cracker already referred to in this *Bulletin* (1909, 7, 386) could be used for this purpose, but large scale trials are required before the

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machine can be definitely recommended. The seeds would afterwards have to be picked out by hand.

In view of the fact that a very large quantity of seeds would be available if the pods were used commercially for tanning purposes, investigations have been made as to the possibility of utilizing them.

The seeds are dark greenish-brown in color, almost spherical, and average about 1 centimeter in diameter. They were found to consist of equal parts of kernels and shells.

The kernels contain only about 26 per cent. of oil, or about 13 per cent. expressed on the whole seed, and it is very unlikely that the oil could be profitably extracted unless the seeds were obtainable at a very low price, especially as, owing to the hard nature of the shell, the residual "cake" would be unsuitable for use as a cattle food.

DRESSING PIG SKINS.*

By I. E. Morton.

Pigs skins are, almost without exception, tanned with oak bark, and require a light preparation for dressing. They are, as a general rule, shaved by hand, lightly boraxed, washed, scoured, washed, and sumaced, washed, struck out, set and strained. Should the skins be required for color work, the straining is done after the dyeing. They must on no account be tallowed before dyeing.

London Color.

For this shade the skins should be well sorted to obtain an even batch. The next operation is staining, which, as a general rule, is done with an annatto, either in an alkaline or alcoholic solution. Annatto is not soluble in water alone, and will only dissolve when boiled up with an alkali, such as soda or borax, or in methylated spirit. It must be borne in mind that annatto is very fugitive to light, and the color obtained by using it will soon fade completely away under certain conditions of light..

Weak phosphine used to be employed for staining, but has

* *The Leather World*, March 11, and April 15, 1915.

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gone out of favor owing to its price; a great asset was its power of coloring beautifully level. Any of the following dyes may be used, and possess the advantage of being at least 200 days fast to light:

Golden brown Y, Cuba yellow, croceine AZ, phosphine substitute (Claus & Reè), tartrazine (Sandoz Chemical Co.), turmeric substitute, sun yellow G, titan yellow Y, titan orange, resorcine brown (all Read, Holliday & Sons).

Method for London Color.—Wet down, strike out well on both flesh and grain, and hang up to dry, and when in suitable condition set thoroughly.

A quarter of an ounce of any of the above dyes is dissolved and made up to 1 gallon, and this is kept as a stock solution. A tub of gum tragacanth is then made up by dissolving 6 pounds in about 60 gallons of cold water, to which has been previously added 4 ounces of oxalic acid, which latter creates a slight fermentation.

The gum takes about a week to dissolve, so that it is necessary to have two tubs, and to have one ready by the time the other is empty. The dissolving can be quickened by boiling, but the gum seems to work smoother if it has been dissolved cold.

Sufficient of the dissolved gum is taken out (about 2 pints), ½ pint of the dye is added, and the whole made up to 4 gallons with water. The skins are next given two good brushings, and horsed up until a quantity have been stained. Hang up to sam, and set when in a suitable condition—that is, neither too wet nor too dry.

The next operation is the hand-stuffing, which is performed by brushing the grain side with dubbin, composed of cod oil and tallow, taking care to give more grease to the hardest parts. The skins are then hung up and dried out in a cool place.

When dry, trim and slicker whiten on the flesh side, which removes any dirt they may have acquired in the first instance, and gives the flesh a better appearance.

After slicker whitening, the skins are pebbled by hand on the grain side, and are then grained up in almost any direction, as a pig skin has no particular shape of grain, like a goat skin. The general rule is to grain them neck to butt and belly to belly.

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They are then flattened out by graining on the flesh side, using a thin rubber board, and are finally brushed with a good stiff brush on the grain. For a bright face they can be brushed over with paraffin wax in the same manner as cleaning shoes.

Some curriers prefer to leave the slicker whitening until the final operation, and, if anything, this is the best plan. After the slicker whitening, the flesh is glassed.

The goods are now ready for resorting, and the light colored ones are rejected and restained; but if the sorting has been done thoroughly before staining, this should not be necessary. If it is necessary to restain the light ones, an alcoholic solution of any basic dye, similar in color to the dye used in the first instance, is used. This is the sole reason why annatto and saffron are such favorites with curriers, as they prefer to curry the goods before staining, and the annatto as bought being an alkaline solution, stains readily enough. The method is all right when working for stock, but if working for orders it is far preferable and quicker to do the currying on the stained goods.

After sumacing, washing, and striking out, dye the skins in the drum with a small quantity of any of the dyes mentioned, taking care when acid dyes are used to use an equal amount of 90 per cent. formic acid to the weight of the dye.

A suitable mixture would be 8 ounces of tartrazine, 8 ounces resorcine brown, 16 ounces formic acid for three dozen medium sized pig skins. After dyeing for about an hour, run off the whole of the water by knocking the pegs out, and well wash whilst the drum is in motion. Allow all the water to run off, and examine the skins. They must be warm for the stuffing, or they are of no use, as cold goods will not take grease. A good stuffing mixture can be made by melting together six parts of stearine, two parts of hard tallow, and two parts of cod oil; or five parts stearine, one part paraffin wax, two parts cod oil, two parts degras. The amount of stuffing to use will vary according to the nature of the skins. A good plan is to use half the quantity of stuffing to the dry weight of the goods, when, if not sufficiently greasy, more can be added; but it is essential to remember that the goods must not be too damp nor too dry, and that the drum itself must be warm.

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After stuffing, horse up overnight if possible, and in any case for at least 3 to 4 hours. Hang up to dry in a cool place; set when in condition, and proceed as for hand stuffing.

A slicker with a phosphor bronze blade has been recommended to the writer, but he cannot say that he has ever used one made from this material. It is very hard, and said to impart a better face to the goods than the ordinary pebble slicker.

The goods, after striking out, can be dyed in the tray, the paddle, or the drum. For preference the paddle is chiefly used, as the goods do not require handling, and can be watched during the dyeing. In the writer's opinion, paddle dyeing is cheaper than either the drum or the tray.

The chief colors required in the pig skin trade are yellows and tan browns for pocketbook work, leggings, note cases, etc. One dozen dyed in the tray for the ordinary brown shade required 2 ounces resorcine brown, 1 ounce tartrazine, 1 gill of a 1 per cent. solution of acid green, and 3 ounces of sulphuric acid.

Fifty skins dyed for a similar shade in the paddle required 4 ounces resorcine brown, 8 ounces tartrazine, $^1/_{14}$ ounce acid green, 1 pint of vitriol.

The amount of dye used in these recipes is practically equivalent, as 12 ounces of dye were used for 50 skins in the paddle, and 3 ounces (or one quarter) for 12 skins in the tray. The only advantage the tray possesses over the paddle is that the skins can be paired flesh to flesh and dyed in this manner, and so a cleaner flesh is produced.

All dyes are dissolved by pouring boiling water on to the dry dye, with the exception of auramine and quinaline yellow, both of which are best dissolved with water at a temperature of 180° F.

The writer has come across dyers who still dissolve their dye up under the steam pipe. This is wrong in two ways; the rust on the steam pipe precipitates basic dyes, and the same class of dyes are precipitated with boiling, which means that the biggest part of the dye is wasted, and does not go on to the leather at all.

In factories where the water is limey it is better to neutralize this by adding a small quantity of acetic acid to the water previous to adding the dye, more especially if the skins are to be dyed with basic colors, as these are precipitated by lime.

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Here follow a few practical recipes, which can be used without any fear of their being unsuccessful, and were used by the writer for years in a factory where flaming in was practically not allowed:

TAN SHADE IN THE DRUM
(50 Skins).

3 lbs. Tartrazine (Sandoz)
6 ozs. Resorcine brown (R. H. and S.)
4 ozs. Sulphuric acid, by measure
24 ozs. Formic acid, 90 per cent.

BROWNS MEDIUM
(50 Skins).

14 ozs. Tartrazine
14 ozs. Resorcine brown
2 ozs. Sulphuric acid
10 ozs. Formic acid

BROWN (50 in the Paddle).

42 ozs. Resorcine brown
8 ozs. Turmeric yellow
1/14 oz. Acid green
7 ozs. Vitriol

LIGHT GREEN (50 Skins),
Drum.

28 ozs. Acid green
12 ozs. Tartrazine or turmeric yellow
20 ozs. Formic acid
8 ozs. Sulphuric acid

MEDIUM GREEN.

28 ozs. Acid green
10 ozs. Tartrazine
10 ozs. Orange
10 ozs. Orange
26 ozs. Formic acid
8 ozs. Sulphuric acid

DARK GREEN.

40 ozs. Acid green
20 ozs. Resorcine brown
2 ozs. Acid red
30 ozs. Formic acid
10 ozs. Sulphuric acid

50 MAROON.

20 ozs. Cardinal red J. (R. H. and S.) or Roxaline (Sandoz)
15 ozs. Fast brown
15 ozs. Bordeaux extra
35 ozs. Formic acid
10 ozs. Sulphuric acid

50 BLUE.

32 ozs. Water blue
8 ozs. Acid violet B.
1/3 oz. Acid green
32 ozs. Formic acid
8 ozs. Sulphuric acid

50 BLACK.

6 lbs. Acid black, such as naphthylamine black nigrosine ..... 3/4 hr.
40 ozs. Formic acid ..... 3/4 hr.
3 lbs. Leather black or corvaline..... 1/2 hr.
6 ozs. Auramine II ..... 1/2 hr.

METHOD OF DYEING.

Get the drum or paddle ready at a temperature of 130° F. Place goods in, and run 5 minutes. Add the dissolved dye through the sieve in two lots; run 10 minutes, and add the diluted acid, and run for 45 to 60 minutes. Wash, horse up, and strike out; when in suitable condition, set, or, better still, nail on the

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boards. For most colored work pig skins are sized on the flesh with Irish moss or linseed mucilage before nailing on the boards.

To anyone not accustomed to striking pig skins out it will be a difficult matter to get them flat. The great secret is to have the skins in a very wet condition, much damper than for striking Persians or calf out.

Finishing.

When dry, trim. Season heavily, using albumin and milk, and a little of the same color which has been used in the dyeing. Grain whilst in a damp condition. When sufficiently dry they are ready for glazing, and a good plan is to use a toothed agate roller instead of a plain glass in the machine; this considerably helps to make the graining easier. After glazing they are broken down on the grain side, and then grained in the ordinary manner from neck to butt and belly to belly. They are then brushed over with Irish moss on the flesh side and hung up to dry, and finally lightly glassed on the flesh. If they are not required glazed they are pebbled by hand on the table, grained, and brushed.

Pig skins are best dyed with the so-called "acid" colors, which give a much more even and cleaner result than when the basics are used. The latter class as a rule dye the flanks a darker color than the middle. Occasionally skins are required to have the well-known Russia smell imparted to them; this can be done in different ways, but it must be borne in mind that the birch tar oil used darkens the color considerably, and allowance should be made for this by the dyer. The best way, in the writer's opinion, is to spray a mixture of birch tar oil and whale oil on to the skins when they are hanging up, using an ordinary hairdresser's spray. A good way also is to make an emulsion of Irish moss and birch tar oil, and apply to the flesh side with a brush.

Pig skins are sometimes required very greasy for saddles, and these are made by staining as for London color, and soaking in linseed oil three or four times, and pebbling between each immersion, and then drying out slowly.

Grain-skived seal is also used for placing as a lining between two pig skins, and is curried whilst damp with cod oil and tallow heavily.

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DEGREE OF TANNAGE.*

By Walter James.

The "Degree of Tannage" of leather is a calculated figure which is usually applied to sole-leathers, whereby the extent or degree of tannage is ascertained. This is obtained by making a complete analysis of the leather, as follows:

Fat .....
Moisture .....
Water soluble matter .....
Fixed tannin .....
Hide substance .....
Insoluble inorganic ash .....

Total = 100 per cent.

The calculation: $\frac{\text{Fixed tannin}}{\text{Hide substance}} \times 100$, giving the "degree of tannage."

It was pointed out by J. G. Parker and M. Paul some time ago that it was necessary to determine the "insoluble inorganic ash," as otherwise, by including the total inorganic ash, an error was thereby introduced; the "soluble inorganic ash" being subtracted twice. The "fixed tannin" figure above includes "combined tanin" and "organic insolubles." The "organic insolubles" would usually be "bloom," or difficulty soluble tannins. Whether these can be legitimately included in the "fixed tannin" figure is difficult to say. In many cases these "organic insolubles" only arise from the ordinary processes of tanning and, in this case its inclusion as fixed tannin would appear to be justified. In other cases such as where leathers have been brushed over on the flesh side with a liberal amount of bloom, etc., its inclusion in this figure can hardly be considered correct. It is possible to treat a sole-leather with bloom in the above way, and increase the "degree of tannage" considerably.

The above remarks apply equally well to any "organic insolubles." At the present time the writer knows of no substances other than bloom, difficultly soluble tannins, reds, etc., which are used in this way but it is quite conceivable that other similar materials are used in this manner. In the determination of

* *Collegium* (London Edition), March, 1915, pp. 76-7.

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"water soluble matter" the extracted portion is filtered before evaporation. This portion often contains considerable amounts of bloom or allied bodies. Where this bloom is mechanically applied it is easily removed in soaking, by the boot manufacturer or boot repairer, or is washed out when the leather is in wear as a boot. It would appear therefore to be incorrect to include this in the "fixed tannin" figure or give it the same value as those "insolubles" which are not so easily removed, and which are present in leathers tanned in the ordinary way.

It is difficult to suggest a method which would overcome this difficulty. Instead of filtering the extracted portion and determining "water solubles," the extracted portion could be evaporated without filtration and the result stated as "water extracted matter." This method, if not quite correct, would at least ensure those leathers mentioned above having a "degree of tannage" which is more in relationship to their value.

The writer would draw the attention of "The Leather Analysis Commission" to this very important point, which requires careful consideration.

ARTIFICIAL BATES.

By J. T. Wood.

Some new artificial bates have been lately put on the market and it may be of interest to give the result of the writer's examination of two of them. The first of these, "pilos," is of Italian origin. It is announced as "the greatest discovery affecting the leather trade since the introduction of chrome tanning, the only product that successfully and advantageously replaces, both technically and economically all puers used up to the present, no matter whether natural ferments, such as excrements, bran, etc., or the chemical ferments at present on the market." From this glowing introduction one would expect that some great step in advance had been made. An analysis of a sample marked Pilos No. 1 showed it to contain about 80 per cent. ammonium chloride

* *Collegium* (London Edition), March 1, 1915, pp. 82-85. Somewhat abriged.

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intimately mixed with some insoluble matter consisting mostly of woody fiber.

Tested for enzymes by the method described in *Collegium*, 1913, p. 44, no tryptic enzymes were found. Lipolytic or fat splitting enzymes were looked for by the method described in the above named paper and also by Kanitz's method. In both cases negative results were obtained.

The brochure issued by the vendors states that "pilos entirely destroys all fats and greases contained in all kinds of skins, thus obviating the necessity of producing a variable percentage of fat or greasy skins." The directions for sheep skins are as follows: "For 100 kilos wet pelt; after fleshing the skins are washed for 20 minutes in water at 39° C. (103° F.). The first bath consists of 11 gallons of water and 400 grams pilos. The temperature on the introduction of the skins should be about 39° C., the skins remaining in the bath 3½ hours. They are then thrown into the paddle at 38° C., and 400 grams pilos No. 2.* The movements of the paddle are alternated with periods of rest. Always decant the clear solution of the small (pilos No. 1) bath, and add pilos in the proportion of 8 grams per kilo, or 1½ ounces for every gallon of water necessary to make up to the original 11 gallons, this bath will serve six or more times. The large bath will last very well for 12 times, without the addition of anything. Cost about 6d. per 100 pounds pelts."

The method cannot be described either as simple or cheap. In the first place, two paddles are required, and the skins must be transferred, involving additional labor.

As regards cost, 100 pounds of pelt would be equal to about 3 dozen average sheep, so that the cost would come out at 2d. per dozen, or twice the cost of the best puer, and over 1½ times the cost of erodin or oropon.

These criticisms are, however, not condemnatory if the bate fulfilled the claims made for it, especially with regard to its action on the fat of the skins. The writer does not find these claims substantiated. Sheep skins treated according to the above directions were found to be about as greasy as those treated in

* Pilos No. 2 appears to be similar in composition to pilos No. 1, but contains more ammonium chloride.

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ordinary puer, while the length of time required in the pilos bate is considerably longer than that necessary for the puer.

The second bate is of English manufacture known as "enzo" and described as follows: "'Enzo' a substitute for the bate or puer. 'Enzo' will be found to give results comparable with those obtained by the nauseous puer, at less expense and greater uniformity of result. A scientifically prepared product that is always of uniform quality, and which depends on bacterial and enzymic activity for producing that properly pulled down flaccid state of the pelt necessary to the obtaining of a soft smooth grained well-tanned leather."

"For every 200-pound weight of fleshed pelt, place 1 pound of 'enzo' in a wooden vessel, and add about 3 gallons of water at a temperature of 95° F. (35° C.). Stir thoroughly until well mixed and allow to digest overnight. The limed goods having been washed and preferably slightly delimed with formic, boracic, or hydrochloric acid, are placed in a paddle filled with water at 98° F. the 'enzo' mixture is added, and the goods paddled until quite pulled down and flaccid. On removal from the 'enzo' solution the goods should be preferably paddled for a short time in tepid water, after scudding and before placing into drench or tan."

An analysis of "enzo" gave the following results:

	Per cent.
Moisture	3.4
Ammonium chloride	68.7
Alkali chlorides (potassium and sodium)	3.5
Alkali phosphates	0.5
Gelatin and proteids	8.4
Fatty matter	0.6
Starch	15.0
Cellulose	traces
Glycerol	traces

No tryptic enzymes were found, but diastase was present. The bate is, therefore, a deliming material, combined with a drenching material, and as such, is, of course, capable of giving good service in the preparation of skins for tanning, but it cannot act in the same way as an excrement bate. A small quantity of an aromatic compound, nitro-benzene, or benzaldehyde, is present, but not in sufficient quantity to be estimated.

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In considering artificial bates, we must distinguish between those which are intended to reproduce the action of the dung bate, and which consequently contain tryptic enzymes, and those which are merely deliming agents, or have an action comparable with that of the bran drench. It is now 16 years since the writer first published his views on the theory of the dung bate. They may be briefly summed up thus: The action of the dog dung bate is due to the action of enzymes in combination with organic compounds, amines and salts of ammonia. The character of the principal enzyme in the dung is a proteolytic one, *i. e.*, it resembles the trypsin contained in parcreatic juice. Numerous researches since carried out have all confirmed this theory, and important practical results have been obtained in the manufacture of artificial bates based upon it. Thus an artificial bate, which is intended to have a similar action to the puer, should be composed of some ammonia compound, and a tryptic enzyme. This is usually combined with some inert "carrier," such as kaolin or wood dust, as the action is found to be accelerated by the presence of suspended solids.

Recipes have been given in the author's book "The Puering Bating and Drenching of Skins," *Spon* 1912, pp. 187, 188, which will sufficiently indicate the practical application of the theory. Practical and scientific tanners know that quite good results may be got without the use of puer for certain purposes, and in many cases a deliming agent followed by drenching will give excellent results, but when the peculiar action of dog puer is required, some tryptic enzyme must be present.

Enzymes, of which so much mention has been made, are produced solely by living organisms, indeed life itself is dependent upon them. We are now able to make use of them in a variety of ways, and surely one of the most extraordinary is their application in the manufacture of bates.

No artificial bate possesses the *whole* of the properties of puer, owing to the presence in the latter of certain compounds in extremely minute quantities which have some effect on the bating action. It is next to impossible to detect these bodies by chemical methods, in some cases, however, their action is known to be due to the influence they exert on the growth of certain bacteria.

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These bacteria secrete various enzymes which exert a bating effect.

Notwithstanding this difference the artificial bate has the advantage that we can modify it and render it suitable for any particular class of work. Thus a bate for a thick calf skin requires to act more gradually than one used for sheep, and a puer for kid or goat on the other hand must have a more powerful "bringing down" action. In other words in the construction of a rational artificial bate it is necessary to have in mind exactly the properties of the finished leather which are required.

REFERENCES.

1. The nature of enzyme action. W. M. Bayliss (Longmans, 1908).
2. Verfahren zum beizen von Häuten. Otto Röhm (*Collegium*, 1909, p. 58).
3. La chimie de la matiere vivante. J. Duclaux (Felix Alcan, Paris, 1910).
4. Bacteriological and enzyme chemistry. Gilbert J. Fowler (Arnold, 1911).
5. Some notes on the enzymes concerned in the puering and bating process. J. T. Wood and D. J. Law, *J. S. C. I.*, 1912, p. 1105.
6. Further notes on enzymes. J. T. Wood, *Collegium*, 1914, p. 123.
7. The puering, bating and drenching of skins. J. T. Wood (*Spon*, 1912).

CHROME LEATHER DEFECTS.*

By Alfred Seymour-Jones.

For good or for evil, the chrome tannage has come to stay and finds its place among the standard tannages—a place awarded by the general public according to the character of the production. Unfortunately, it is only too true that much of the chrome leather offered for sale to-day is unworthy of the name, and has brought discredit upon a young industry. Why is this so? What are the reasons? Against this low grade of chrome leather it is not only difficult to find a market for the high grade, but when found there is little or no profit in it. The salesman of high grade chrome leather finds it of little avail to extol his wares when the buyer produces the low grade and low-priced chrome leather with the statement that "it makes up all right"—into boots, for

* *Leather Trades Review*, April 21, 1915, p. 220.

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example, regardless of the wear to the general public. It will be clearly seen that I do not indict chrome tanning *per se,* but I do blame those chrome tanners who are bringing discredit on the industry. This I believe to be true to certain causes all of which might have been avoided.

First of all I will deal with the failures of chrome leather. It will be quite impossible to traverse the entire field within the limits of this article, and I will therefore take the case of the wholly chrome leather boot, and try to explain, as far as possible, in non-scientific terms, the causes of some failures.

The following charges have been made against the chrome boot, both as to upper and sole:

(1) The chrome leather football boot may remain water-proof for the duration of a match, but in some cases it becomes more and more sodden as the game proceeds, until it is quite "tripey" at the end of the match, and the feet are wet. On drying, in spite of lasts or trees being inserted, it dries hard, and if no lasts are inserted it dries "all shapes," and, in most instances, it shrinks.

(2) During the war chrome boots have been served out to the army at home and in the trenches. The men complain that they are not water-proof, draw the feet, dry out hard, shrink, refuse to take grease, and are cold to the feet. They implore their quartermaster to give them the regular army kip boot. Why?

Without adding to the indictments, it is only fair to the soldier to add that, generally speaking, he knows little about leather—he simply judges by results. He finds that the boot which fails differs in color—internally—from the regulation army boot, and refers to it as "green leather"—a very apt trade term, as I shall prove.

It is necessary to examine these indictments carefully. To do this, examination must be made, with the aid of the microscope, of sections cut from sound vegetable-tanned, sound chrome-tanned, and unsound chrome-tanned leather, and further tests must be made by chemical analysis.

If a section of sound vegetable-tanned leather be examined under a low power it will disclose a close union between tannin and gelatine—that is, they have chemically combined throughout the entire fibrous mass; but a section of partially tanned (vege-

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table) leather shows that the unification is proceeding by penetration of the tannin between the fiber bundles. This tannin slowly penetrates the bundles and finally the fibers themselves, until an equilibrium is established between the gelatine and tannin compound, approximately 50 per cent. each way. If this point is passed the tannin may be seen packing itself between the coarser fibers, giving the effect of "loading."

A section of properly tanned chrome leather discloses the interesting fact that the fibers are "plated" with oxide of chromium, leaving the interior structure still free gelatine. In badly chrome-tanned leather this "plating" is not only less heavily deposited on the coarse fibers, but also absent on the internal and smaller fibers, clearly indicating under-tanning. All the sound chrome-tanned leathers I have examined contain above 7 per cent. of chromic oxide, but many of the unsound chrome leathers contain as little as 2 per cent.

This under-tanning may be proved in another way. Prepare a solution of equal parts of acetic acid and glycerine, cut small pieces of properly tanned (vegetable) leather and chrome leather for examination, divide the solution and place the two pieces separately in glass vessels, and let them stand for a week or two. It will be found that the properly tanned vegetable leather will remain unaltered, whereas the chrome (if under-tanned) will have swollen and become soft, showing the presence of free gelatine.

The practical man will readily admit that any form of under-tanned pelt will cause boots to dry hard, shrink and become "tripey," and that these defects are absent in sound leather, which will absorb grease under given conditions.

It has been claimed for chrome that it is a rapid tannage. This is true in a comparative sense only. Unfortunately the non-scientific chrome tanner often disregards this characteristic, and assumes that when the hide or skin is "blue through" it is completely tanned. Herein lies the failure. The only test is that of analysis by a chemist. Current ideas in regard to the color and rapidity of the chrome tannage are difficult to eradicate. The practical man assumes too often that when a pelt is blue through it is not only tanned but incapable of being further tanned. To

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prove that this suggestion is wrong, the writer many years ago fastened some pieces of hide in a chrome tanning drum and left them exposed to tan liquors for nearly two years. When finally removed they were hard, solid pieces of matter, and were found on analysis to contain 84 per cent. of chromic oxide. The value of this experiment lies in the fact that it definitely proved that chrome tanning followed similar principles to those of vegetable tanning. It is not necessary to enlarge on this; suffice it to say that it is absolutely necessary to-day to employ a chemist in the tannery to control the operations if success is to be secured. If a chemist is on the ground and enjoys the confidence of his employer the tanner will reap his reward by seeing the present complaints a feature of the past.

One word more on the topic of chrome tanning. The average tanner relies upon the boiling test to indicate whether a pack of skins is sufficiently tanned or not. This is a poor aid, and is as likely to mislead as not. There are physiological and physical circumstances which operate against it proving true in every case, and all boiling tests should be supplemented with chemical analysis.

The charge that chrome leather is cold is only too true, and the metallic peculiarity of the tannage makes it so. The only remedy appears to be a vegetable or linen lining and a warm sock.

The complaint as to perspiration is also true, but is a matter of degree and personality. It arises from two main causes, excessive perspiration and fetid perspiration. In either case both are most distressing to the person and destructive of leather. As a rule perspiration is alkaline, and is composed of common salt and fatty acids, which are in turn decomposed by the heat of the body and bacterial action into alkali. There are many remedies to be purchased to allay this evil. One has been recently placed on the market in America by the Pfister & Vogel Company, under the title "Hybro," which is composed of 10 parts perborate of zinc, 10 parts perborate of soda, and 80 parts powdered talc. These are well mixed and applied, and may also be dusted into the shoe.

The main trouble to-day with the average chrome leather produced is the lack of a true relation of chromic oxide to gelatine

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as to penetration, combination and proportion. These factors can only be satisfactorily solved by employing some chemical and physical control, and when solved, by permanently employing a chemist to control the various operations.

ABSTRACTS.

Chrome Leather Defects. Letter by W. S. GREEVES to the *Leather Trades' Review,* April 28, 1915. The very able article by Mr. A. Seymour-Jones ought to be of great value to every tanner who has an interest in upholding the reputation of chrome leathers, and giving to the public a comfortable, and at the same time the most durable, leather that can be produced. In the early days of the industry fortunes were lost by under-chroming, and many thought that a light tanning without filling was quite enough, and that 2 or 3 hours in a drum was all that was required. Even to-day there are many makes that would give under 2 per cent. of chromic oxide, but the best Continental leathers contain an average of 5 to 6 per cent., and are more heavily fat-liquored. The more a leather is tanned the more fat-liquor will it require, and the better will be the penetration. The exhaustive trials made on the leather tire for automobiles were a very fine education for those who made a study of what could be done to give the utmost resistance to wear. The conclusions of the various tests were summarized as follows: The heavier the leather was tanned the less stretch it gave; it kept its substance better, and in conjunction with more fat-liquor was very much more resisting to friction. To get a well-filled leather the liquors should be as nearly neutral as possible. Acid liquors penetrate too rapidly, and do not adhere to the fiber in any proportion. A basic liquor has the defect of tanning too heavily on the surface without penetration. A few hours gained in time is bad economy for those who wish to produce a high-class article, and it is especially useful at the present time to bear this point in mind when all are liable to hasten good action.

Chrome Leather vs. Vegetable-Tanned. Vigorous discussion of the relative merits of chrome and vegetable leather for shoes has been going on in the English trade papers. In the *Leather World* for Feb. 11, John R. Blockey takes up the defence of chrome tannage. In the Mar. 11 number W. James and P. R. Barker reply, and in the issue of Apr. 15, Mr. Blockey comes back with a rebuttal. Mr. Blockey first calls attention to the fact that much of the outcry against chrome leather is based on mere rumor, and that few proved cases of defective chrome shoes do not afford any basis for a fair comparison, since so many other factors beside the mode of tannage of the leather would have to be considered. He suggests that the only way to arrive at a fair comparison would be

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to examine a large number of pairs of each kind of shoes, and take some sort of an average. He remarks that many statements have been in circulation in regard to chrome leather which are manifestly false. Of these the most absurd is the claim that chrome leather rots. Chrome leather resists heat and decay much better than vegetable tanned. Its wearing qualities are admitted even by its enemies. With regard to the action of water, vegetable tanned leather which is repeatedly wet and dried again becomes brittle and hard. Under the same circumstances chrome leather retains its suppleness and its shape. The fiber does not absorb water. In order to prevent vegetable leather from becoming stiff after it has been wet, grease must be applied. The fact that chrome leather does not have to be greased to keep it soft causes neglect, and the endurance of the leather is less if it is not occasionally greased. The fact that chrome soles water-proofed with wax, etc., are less warm than those tanned with bark is due to the filling of air spaces with wax, thus making the leather a poor non-conductor.

Messrs. James and Barker remark that a fat-liquored chrome leather is not water-proof, but permits the passage of water from wet grass even. To this Mr. Blockey replies that in order to make any leather water-proof it must be stuffed, and that a stuffed chrome leather is just as water-proof as a vegetable one. Many words are spent on both sides on the matter of cold feet, which matter being a personal one, is not of sufficient general interest to consume our space. Messrs. James and Barker attribute the acknowledged wear-resisting quality of waxed chrome to the wax and not to the leather. To this Mr. Blockey makes the obvious retort that his opponents can easily satisfy themselves by trying a pair of paraffin soles. Messrs. James and Barker wind up with the following general observations: "In further support of what we have affirmed, can be put forward the fact that the advent of chrome upper leathers resulted in the introduction of the light artistic boot. In this sense there is no doubt it will continue to be important, but for rough usage it cannot give the same value as vegetable curried leathers. In the case of the man who can afford many pairs of boots and therefore many changes, such disadvantages as we have stated are reduced to a minimum; but in the case of the majority of the workers, who wear one pair of boots repeatedly, with occasional change for Sundays, such disadvantages are increased, and for them there can be little doubt vegetable tannage is far ahead of chrome. The popularity of chrome has been brought about by the demand for cheaper leathers, and subsequent cheap boots of smart appearance, rather than by any other inherent and advantageous superiority." Mr. Blockey mercifully refrains from any comment on "advantageous superiority," but contents himself with the general statement that heavy stuffed chrome uppers, so far from being inferior to the corresponding type of vegetable leather, are quite as water-proof, and better in the matters of keeping shape and resisting wear. (See preceding article by Alfred Seymour-Jones and a further abstract, p. 335.)

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Tanning Solutions and Antiseptics. ANON. *Conceria*, **22**, 247. The author discusses the cases in which tanning solutions are employed under conditions which fall short in varying degree of being antiseptic. Tannin itself acts as an antiseptic for many micro-organisms; certain of the latter, however, especially those which may be classed under the general head of moulds, are resistant to the action of tannin. The most objectionable of the above micro-organisms are those which grow upon the surface of the tanning liquor and produce a relatively large amount of oxygen with consequent oxidation of certain constituents of the tanning material; these micro-organisms are injurious in the highest degree to tanning solutions. The antiseptic action of tannin is in many cases assisted by the action of certain acids which are naturally present in tanning solutions. A consideration of the general question of the antiseptic action of tanning solutions is complicated by the great number of unknown factors which play a part therein and by the fact that the data so far accumulated only apply for the most part to special cases. H. S. PAINE.

Ultra-violet Rays in the Leather Industry. ANON. *Conceria*, **22**, 356. In addition to other industrial applications of ultra-violet rays, such as the destruction of bacteria, sterilization of water, etc., the use of ultra-violet rays in the leather industry in the manufacture of varnished leather is discussed. Instead of exposing the treated surface to the rays of the sun, as in the old process, the light from a mercury lamp is allowed to fall upon this surface in a relatively small, enclosed space. One disadvantage of this process, as first carried out, was due to the fact that ozone produced by the mercury lamp had an injurious action on the varnish. This objectionable feature has been obviated to a great extent by removing water vapor from the air which enters the treating chamber. H. S. PAINE.

Degreasing of Hides by a Wet Process. ANON. *Conceria*, **22**, 337. The series of non-inflammable products obtained by the substitution of chlorine in the paraffin and olefine hydrocarbons may find an extensive application in the removal of fat from various hides. Tetrachlorethane is the most frequently used of these compounds, but pentachlorethane and di-, tri- and tetra-chlorethylene may also be employed. The solvent is mixed with water at 35°-40° C. and the green hides are worked in the mixture until the fat forms a colloidal solution which separates on cooling; the solvent may then be recovered by drawing off and filtering. In one instance 10 dozen ram skins were treated with 20 kilos of tetrachlorethane and 80 liters of water at 40° C. After 2 hours the fat was practically eliminated and the hides were removed; liquid fat collected at the surface of separation of the water and tetrachlorethane on cooling. The solvent was then drawn off and the last traces of suspended fat were removed by passing through a filter press. The hides were then washed with water and another portion of solvent and the fat which was removed was recovered in the usual manner. The above process should

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be conducted in the dark to as great an extent as possible, inasmuch as light has a decomposing action on the chlorine substitution products used in this method of degreasing. H. S. PAINE.

Chrome-tanned Calfskins. ANON. *Conceria*, **21**, 507. The author emphasizes the important part which the initial choice of material plays in the manufacture of leather from chrome-tanned calfskins. Small skins of fine grain and texture yield better leather than large skins. Thin skins with thick neck portions are never satisfactory because the large veining renders it impossible to work them except with great difficulty and detracts greatly from the appearance of the leather. Green or salted skins are better than dry skins, since the latter are ordinarily flaccid and without strength of grain, while the flank and belly portions are not usually sufficiently clean and thin. Calfskins require more accurate treatment in the laboratory than any other kind of skins and are most difficult to tan properly. H. S PAINE.

Pure Salt for the Preservation of Hides. ANON. *Conceria*, **22**, 332. An English patent (18-1890, 1913) based on the Abt theory of the inorganic origin of salt spots has recently been issued; the procedure involved requires the use of practically pure salt. According to the theory, the substance of the hide, because of its colloidal nature and amphoteric property, absorbs the salts of magnesium and calcium which are present in common salt with consequent detriment to the hide and production of spots. By means of a special process it is possible to obtain common salt containing 99.99 per cent. of pure sodium chloride and it is claimed that when this product is used the amount of liquor which exudes from the hide is less than in cases where the impure salt is employed; the amount of alkaline substance dissolved from the hide is also reduced to a minimum. Sodium chloride does not form a hydrate under the usual conditions of temperature and pressure, while the following hydrates are formed by salts which constitute the usual impurities in common salt: $CaCl_2.6H_2O$, $MgCl_2.6H_2O$, $CaSO_4.2H_2O$, $Na_2SO_4.10H_2O$. It is further claimed that the alkaline substance which is formed by the action of pure salt on hides is removed by washing prior to liming, while the amount of nitrogenous material which passes into solution is reduced to a minimum because of the absence of sulphates and salts which form hydrates. When impure salt is used, the above alkaline substance probably reacts with salts of calcium and magnesium with production of complex neutral salts and formation of insoluble protein compounds. The salts of calcium and magnesium are further capable of reacting with the natural fatty substance (a portion of which is present in the form of free fatty acids) of the hide, thus producing insoluble soaps. These soaps, being distributed irregularly in the hide, obstruct the pores, thereby producing spots, as well as a decrease in the volume of leather which is obtainable. If the above claims are found to be justified, this pure salt should find a wide application, provided it can be produced with sufficient cheapness.

H. S. PAINE.

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The Detection of Lactic Acid in Leather, also in Tan Liquors and Other Liquids. R. LAUFFMANN. *Rundschau*, April 8, 1915, Vol. 7, pp. 105-10. Dr. Paessler has recently published a process for the detection of free acid in leather, by which the leather is subjected to dialysis. If the dialyzate has an acid reaction, the leather contains free acid. Organic acids, except perhaps oxalic, are not injurious, but the presence of mineral acids menaces the durability of the leather. It is, therefore, important to learn what kind of acid is present in the dialyzate. If neither SO_3 nor Cl is found in the dialyzate, only organic acids are present. Volatile organic acids may be driven out by heat. If after this treatment, the dialyzate is not acid, no free mineral acid was present; if it is acid, mineral acids or non-volatile organic acids or both are are to be looked for. Oxalic acid may be detected by means of calcium chloride solution (acetic acid having been added to the solution). For the detection of lactic acid, use is made of the fact that the molecule of lactic acid, an α oxy-acid, under the action of certain oxidizing agents or acids, suffers a splitting up, one of the products being acetaldehyde, which may be detected by appropriate reagents. The decomposition of lactic acid may be accomplished by boiling with peroxide of lead or of hydrogen or with certain mercury salts, producing acetaldehyde and carbon dioxide; or it may be boiled with a mixture of concentrated HCl and dilute H_2SO_4, producing acetaldehyde and formic acid, or with concentrated H_2SO_4, producing acetaldehyde, CO_2 and water. There are many tests for acetaldehyde; seven are given. The two which were found most suitable are: (*a*) Addition of a few drops of a water solution of diethylamine and of a very dilute solution of sodium nitroprusside to a solution containing acetaldehyde gives a deep-blue coloration. (*b*) If iodine be added to a solution containing acetaldehyde and then alkali until the color of iodine is nearly discharged, the odor of iodoform is perceived, and if much acetaldehyde is present, a yellow precipitate of iodoform appears. In general, treatment with lead peroxide is more satisfactory than the acid methods for splitting the lactic acid, since many of the substances which may be investigated for lactic acid yield acetaldehyde on boiling with acid even if no lactic acid be present. Boiling with acid is also liable to produce formaldehyde and furfurol, and these mask the tests for acetaldehyde. If the substance to be tested contains mineral acid, the quantity should be determined, and before beginning the distillation with lead peroxide, enough Na_2CO_3 is added to neutralize the mineral acid. Tanning extracts may be made up by diluting 100 grams to 1 liter and taking 25 cc. for a determination. This quantity is heated with lead peroxide and the distillate passed drop by drop into a test tube containing the mixed diethylamine and sodium nitroprusside. The mixture is made up of 1 drop of diethylamine to 12 drops of water and 5 or 6 drops of dilute nitroprusside solution. After 1 or 2 minutes this mixture becomes blue. About 5 cc. of distillate is collected in the tube. If the distillate is free from acetaldehyde the characteristic blue color of the mixed reagents vanishes during

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the distillation. If acetaldehyde is present, the color persists or passes over into a more or less pronounced violet. Five cc. of distillate mixed with 8 drops of a 10 per cent. KI solution, and enough strong NaOH solution to nearly discharge the color will give the iodoform reaction if acetaldehyde is present. L. B.

Distinction between Chestnut-wood and Oak-wood Extracts. J. JEDLICKA. *Gerber,* Mar. 15, 1915, pp. 85-6. Oak-wood and chestnut extracts behave very similarly toward the ordinary tests. Eitner's reaction with ammonium sulphide does not give certain results. The author used Jean's method (*Collegium,* 1902, p. 283), supposed to be quantitative, and found in pure oak-wood extract 60-70 per cent. of chestnut! For Slavonian extracts he regards the Jean method as useless. The author's method, a modification of Stiasny's, is as follows: To 5 cc. of tan solution, analysis strength, add 10 cc. of 10 per cent. acetic acid, 5 cc. of a 10 per cent. solution of lead acetate, filter, add to filtrate 0.5 cc. 1 per cent. iron alum solution and 0.5 gram crystals of sodium acetate. Chestnut extracts in general give a strong blue-violet color, while oak-wood extracts give a nondescript yellowish color. The author finds the ash content of oak-wood from 1.2 to 1.8 per cent. while that of chestnut is much lower, 0.4 to 0.5 per cent. L. B.

Detection of Cellulose Extract in Leather. R. LAUFFMANN. *Rundschau,* April 22, 1915, pp. 121-3. This is inspired by Dr. Moeller's paper (abstr. this J., May, page 279), in which the suggestion is made that the failure of Moeller's process in Lauffmann's hands was due to the too fine subdivision of the leather used for the tests. L. has now repeated his tests on the same leathers described in his previous paper (abstr. this J., March, pp. 160-5), using samples cut up instead of ground. No reaction for sulphite-cellulose was obtained except with the leathers in whose tannage sulphite-cellulose extract was used. These are numbered 7, 8 and 9. No. 7 was tanned throughout with a mixture of quebracho and sulphite-cellulose, No. 8 was begun with quebracho and completed with sulphite-cellulose, and No. 9 was begun with sulphite-cellulose and finished with quebracho. Four methods were used. The cinchonin method of Appelius (abstr. this J., 1914, pp. 566-7) gave a reaction with all three leathers, less distinct with No. 9 than with the others. Dr. Moeller's first method, in which the leather is extracted for 24 hours with caustic soda, the extract acidified and filtered and then tested by the Procter-Hirst reaction, gave a reaction with all three leathers, most with No. 8. His new method, using alcoholic soda solution, with 3 hours' digestion, hot, gave reaction with 7 and 8 but none with 9. A fourth method used was the extraction of 10 grams of leather by boiling a short time with 50 cc. of water, cooling, filtering and applying the Procter-Hirst reaction to the filtrate. This gave a reaction with all three leathers, most with No. 8. Comparing these results with those given on p. 165 (March number of

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this J.), it is evident that the cut leather gives the reaction much more readily than the ground samples used in the previous work. This is the more noteworthy because the leather had lain some months since the previous tests were made. The author remarked that digestion with NaOH brings out so much material from the leather that it is well to dilute the liquid before applying the test.

From the success of the fourth method, Lauffmann concludes that the extraction of the coarsely cut up leather with alkali is not necessary, but that the extraction with boiling water will suffice to detect sulphite-cellulose used in the making of leather, at whatever stage of tannage it was used, even if the leather has been a long time tanned. He points out in answer to Dr. Moeller that the suggestion in the previous paper in regard to possible change in the chemical constitution of the cellulose extract with time was not an assertion but a suggestion. L. B.

The New Dehydration Theory of Leather Formation as Opposed to the Oxidation Theory. E. O. SOMMERHOFF. *Collegium*, 1915, 26-7. Chemically fixed hydration water is withdrawn from hide albumen by the action of tannins of meri- (partially) oxidized character; the hydrogen acceptor is the colloidal, basic phlobaphene while the complex, soluble, oxidizable tan-acids (developers) constitute the oxygen acceptor. The author through his studies upon chrome tannage was led to substitute the above theory for the oxidation theory of Fahrion and of Meunier.

Hide albumen may be compared with the inorganic mordants such as the colloidal aluminum hydroxide; this, like hide, silk and wool, has both the character of acid and base. Such colloidal hydroxides become inactive and insoluble on dehydration by heat; a method not available with albumin. Neither do neutral dehydrating agents like alcohol, acetone, etc., completely remove the water. Light will dehydrate colloids, but the action is superficial; the sun-dried East Indian hides are illustrations. After a lengthy discussion of the photo-chemistry of the gelatine dry-plate, considered as a superficial tannage, the analogy is extended to tannage proper (internal). Because of the strong chemical affinity of the albumin, the water in white hide is fixed in part in a very reactive state and shows great inclination also to decomposition by freshly precipitated metal colloids, for example, basic chrome sulphate. The decomposition of the water can, however, only take place while hydrogen and oxygen acceptors are present within the mordanted cells; this is only the case with substances of meri-oxidized character (for example, chromic hydroxide + chromi-sulphuric acid). Only such are suitable for tanning agents.

I. $2Cr_2^{III}(OH)_2(SO_4)_2 + NH - R(\text{hide}) + H_2(OH)_2 =$
$[R - NH \ldots . H_2Cr_2(SO_4)_4] + 2Cr(OH)_3.$

II. [*a*] $2(OH)_2Cr^{III}(OH) + H_2(OH)_2 =$
$2Cr^{II}(OH)_2 + 2H_2O + H_2O_2.$

[*b*] $H_2Cr_2(SO_4)_4 + 3H_2O + 3H_2O_2 =$
$2H_2Cr^{IV}O_4 + 4H_2SO_4 + H_2O.$

III. $3Cr^{II}(OH)_2 + H_2Cr^{VI}O_4 + 2H_2O = 4Cr^{III}(OH)_3.$

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Since to tan leather very little chromic salt is required, this acts as a catalyzer in dehydrating the hide albumen. It might be expected that addition of much energy would be needed to split off the water, but on the contrary, the chemical union between hide and hydrate water is very easily loosened and probably only slight amounts of hydrate water are really decomposed. It is possible the above dehydration indicated is only induced and the remaining hydrate water splits off directly as molecular water without decomposition The chromi-sulphuric acid cannot be entirely washed out, for the hide remains green colored. On drying, and especially on stretching, the acid perhaps decomposes with water in the above described manner, forming a coagulated, strongly basic chromi-sulphate suspended in the cells.

In vegetable tannage, the ordinary commercial tannin, pathological tannin from its origin, is likewise for the tanner a sickly product, since in tannage its chief role is only that of a tan-acid, that is, an oxygen acceptor. Its value is better measured by the Löwenthal permanganate method than by hide powder. Only the genuine physiological tannins (polydepsides), such as contain phlobaphenes, are important to the tanner and particularly the bark and wood extracts whose phlobaphenes have a marked oxy-ketone character. In quebracho phlobaphenes for example, the tannophore group CO (ketone) is reduced to the "auxotannone" (aiding tannage) group C-OH. Analogous to the chromic sulphate, the quebracho extract is assumed to be composed of a phlobaphene acting as hydrogen acceptor and a soluble tannic acid (present as glucoside) which acts as oxygen acceptor or developer. These developers are of very high molecular weight and during tannage are burned up in the drum to lower acids (oxalic and CO_2?) partly with great evolution of heat. There is, of course, no means of determining the very important reducing value of a phlobaphene. In measuring the oxidation value of the tannic acid in very dilute solution with $KMnO_4$, the meri-oxidized phlobaphenes are also oxidized. Since the study of logwood dye-stuff has shown that a weakly oxidized phlobaphene is still a good H-acceptor, it is correct to interpret a high $KMnO_4$ consumption as indicating a high tannin content. The hide powder method in combination with the $KMnO_4$ method (in practiced hands) can furnish a sort of measure for the value of a pure tannin extract.

Pure quebracho extract behaves like too strongly basic chromic sulphate, the phlobaphene gel separating too easily. If these difficultly soluble oxy-ketones are treated with $HNaSO_3$, there are probably formed the easily soluble Na salts of the phlobaphenes and the liberated SO_2 hinders the alkaline action of the hydroxyl ions. A great excess of SO_2 is to be avoided since it would disturb the autoxidation of the tanno-glucosides during tannage. The formation of ozone, and therefore hydrogen peroxide, is assumed to take place in the drum. Photo-chemical decomposition of water (autoxidation) takes place very rapidly when a gaseous H-acceptor like oxygen, or better, ozone and a solid gel from

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H-acceptor like tannin phlobaphene is present. In vegetable tannage, the water is withdrawn principally by its decomposition while in chrome tannage the splitting off of molecular water predominates. In quinone tannage similarly very little water is decomposed, but the action of the quinone is catalytic, splitting off molecular water during drying of the hide. Formaldehyde acts like quinone. The polymerized aldehyde changes in alkaline solution to a fructose which is reduced to mannitol and by oxidation of the air again reverts. Formic acid, present originally or formed by oxidation with the air, serves as tan-acid and O-acceptor, yielding CO_2 and H_2O. Chamoisage the author considers similar and hopes to take up later in detail. W. J. K.

Sulphurous Acid in Sulphited Tannin Extracts. CARL SCHIFFKORN. *Collegium,* 1915, pp. 101-8, 146-54. Kerp (*Chem. Ztg.,* 1907, 1058) has made a study of combined sulphurous acid in organic compounds, particularly in wine, and published a resumé of the literature. The organic fixed sulphurous acids are easily soluble in water, less soluble in alcohol. In water they are hydrolyzed according to

$$H_2C(OH)SO_3Na = H_2CO + NaHSO_3.$$

The aldehyde sulphites are the most stable and the glucose compounds are the easiest ruptured, as well as the most poisonous. The organic sulphurous acids resist oxidation, for example, are not affected by iodine in Ripper's method for formaldehyde determination. Kerp has prepared pure the glucose salt

$$CH_2OH - CH(OH)_4 - CH(OH)SO_3Na$$

which reacts acid in solution from dissociation. Recent investigations have shown that glucose is an essential part of the tannin molecule and that tanstuff extracts contain glucosides. The sulphurous acid in sulphited extracts the author believes to be fixed in organic combination and most probably with glucose. Sommerhoff's observation that glucose results on sulphiting quebracho confirms this; the sulphurous acid hydrolyzes the tanstuff and combines with the liberated glucose. The free SO_2 in such extracts results through hydrolysis of the glucose sulphonic acid or action of organic acids upon the bisulphite, or from direct employment as aqueous acid. Sulphates in sulphited extracts may occur as impurities in the alkaline sulphite employed, further as oxidation of bisulphite resulting from hydrolysis of the glucose salt, also from adulteration with $MgSO_4$, finally from Na or Al sulphate used in bleaching some French and English extracts. Fixed sulphates are not injurious but rather promote tannage. Free sulphuric acid can hardly exist in sulphited extracts, since it would react with the sulphites liberating SO_2 or $HNaSO_3$.

Detection of SO_2 in Extracts.—Hitherto the method of Heidenreich has been used. The extract solution of official strength for analysis is detanned, and 100 cc. of the detanned liquor are warmed with 3 grams MgO, filtered, granulated zinc added, then HCl and let stand in a beaker covered with Pb-acetate paper which becomes brown (H_2S) with a posi-

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tive test. Another qualitative test recommended is the use of potassium iodate, liberating free iodine with a limited amount of SO_2; 2-3 grams of extract are quickly mixed with H_2O, and 1-2 cc. 25 per cent. phosphoric acid in a 100 cc. Erlenmeyer flask which is then quickly corked with a strip of iodate-starch paper suspended 1 cm. above the test. If there is no blue after 10 minutes nor after 10 minutes heating on water bath, the tightly corked flask is let cool; if no blue appears after ½ hour standing, SO_2 is absent. Another sensitive test (H. Schmidt) consists in nearly bleaching a dilute iodine solution (in KI) to faint yellow, adding starch and transferring a drop of the blue liquid to the convex side of a watch glass laid over a small dish containing 1-2 grams extract with H_2O and H_3PO_4. In presence of SO_2, the drop is decolorized in 5 minutes; the reaction is forwarded by warming to 40-50°, which is not, however, imperative. To ensure a decolorization not having been due to heat alone, a piece of ice is laid on the watch glass; if the blue color does not return, SO_2 caused the bleaching. The test for SO_2 may also be made by bringing a drop of dilute potassium iodate solution mixed with starch. This becomes a blue which afterwards disappears when much SO_2 is present. Finally both tests may be carried out side by side, one drop bleaching, the other becoming blue.

Quantitative Determination.—I. Total SO_2. (*a*) Gravimetric: Two to 3 grams of extract are dissolved in 200 cc. previously boiled H_2O in a flask with addition of soda to weak alkaline reaction. After 1 hour's standing, the flask is fitted with a doubly bored stopper, through which CO_2 is led to the bottom, the other opening leading to a Liebig condenser, terminating with a U-tube (Peligot) containing 50 cc. I solution (10 grams pure I, 15 grams KI to liter). The stopper is lifted a moment while CO_2 still passes, 10 cc. 25 per cent. H_3PO_4 poured in, stopper replaced and half the liquid distilled off. The iodine solution (which should still be brown) is then acidified with HCl, boiled till yellow color goes (free I dissolves $BaSO_4$) and then precipitated with $BaCl_2$, boiling. A modified method substitutes for the iodine a 3 per cent. solution H_2O_2, 10 cc. in the first receiver, 5 cc. for safety in a second. The sulphuric acid formed can also be first determined in the same test volumetrically by titration with alkali (methyl orange).

(*b*) Volumetric (Schuhmacher and Feder, *Zeit. Unters. Nahr. u. Genussm.*, 1905 [10], 649): The SO_2 is absorbed in a standard solution of KIO_3, the liberated I then expelled and the excess of iodate titrated. The iodate is standardized (after adding excess of KI and H_2SO_4) with thio. The author employs about 3 grams of weighed extract in a distillation flask fitted with doubly bored stopper, condenser and train of two absorption vessels. The second opening of the stopper admits a dropping funnel used first to fill the apparatus with CO_2, then to introduce 10 cc. H_3PO_4, sp. gr. 1.2. The passage of CO_2 is maintained during the distillation. If the volumetric method with use of H_2O_2 be employed, the danger of carrying over H_3PO_4 may be obviated by inserting above

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the condenser a small flask containing beads and warmed on a water bath.

If bisulphite alone had been employed for sulphiting, the total SO_2 found is reckoned as $NaHSO_3$, which is approximately correct. A direct estimation of bisulphite and sulphite in extracts is impossible. Whether bisulphite alone or in combination with sulphite has been used may be deduced from the total SO_2 content when one considers that a maximum of 4 per cent. bisulphite is used in practical sulphiting (based on original extract) and in the second case a maximum of 2 per cent. anhydrous sulphite and 4 per cent. bisulphite. If the total SO_2 content is less than 2.5 per cent., bisulphite alone was probably used; above that, bisulphite and sulphite.

The author has computed an approximate formula for practical use, assuming that sulphite and bisulphite are used in the usual ratio of 1:2. Let Σ = per cent. total SO_2 in extract, x = per cent. SO_2 in sulphite used-y = per cent. SO_2 in bisulphite used; then $x = \frac{\Sigma}{3.42}$, $y = \frac{\Sigma}{1.4126}$. If the addition of anhydr. sulphite in per cent. original extract = a and of bisul, phite = b, then $a = 2.0877x = 0.06097\Sigma$ and $b = 1.71526y = 1.21426\Sigma$.

Free SO_2 Content.—The acidimetric determination by Thuau and Madru after distillation, appears open to objection since the organic combined SO_2 may split off hydrolytically and give too high results. Further, distillation to dryness is necessary to fully expel SO_2 which is highly soluble in H_2O. The author employs a distillation liquid of low boiling point (66°) and indifferent towards SO_2, namely, methyl alcohol. Ten grams extract and sufficient C. P. methyl alcohol are placed in a 400 cc. flask (glass beads promote quiet distillation) fitted with CO_2 inlet, a distillation tube (Schönemann's dephlegmator recommended) and condenser. The SO_2 is collected in H_2O_2; the excess of H_2O_2, CO_2 and alcohol are expelled by heat and the H_2SO_4 titrated (cold) or precipitated as $BaSO_4$. The SO_2 may also be absorbed in standard alkali.

Organic Fixed SO_2.—According to the author's view, this exists as glucose sulphurous acid, but cannot be directly determined; it is found by subtracting free from total SO_2. Since the two forms of acid probably have different action on leather, a separate determination of each would be desirable. W. J. K.

Chrome vs. Bark Leather. The controversy outlined on pages 325 and 326 between J. R. Blockey on the one part and Messrs. James and Barker on the other is continued in the May 13th issue of the *Leather World,* which came to hand since the preceding pages were in type. James and Barker reply at length, explaining several points. They sum up their conclusions thus: "Vegetable leathers as a class, being easily stuffed with greases, are more water-proof than chrome upper leathers, as a class, which are not so readily stuffed. Vegetable upper leathers do not occasion discomfort to the wearer from excessive heating of the feet. The general wearing quality of vegetable upper leather (and in this statement its water-proofness and the avidity with which it will take

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up further supplies of grease, as well as the manner of make-up, must be taken into account) is greater than chrome upper leather. Chrome upper leathers heavily stuffed with grease will be more water-proof while the grease is retained than a vegetable upper similarly stuffed, and will also in this condition wear extremely well; but it will in many cases cause discomfort from excessive perspiration, especially in warm weather, and it will not readily take up further applications of grease, which are so necessary to maintain its water-proofness and wearing qualities."

The Rapid Manipulation of Kjeldahl's Method. A. T. HOUGH. *Collegium* (London edition), May, 1915, pp. 126-7. In view of the fact that the International Commission on leather analysis is now working out propositions for an official method, any means of increasing the rapidity of oxidation of nitrogenous organic matter would seem worthy of attention. The author has had wide experience in leather analysis and has tried most of the oxidizing agents which have been proposed for this purpose. He believes potassium permanganate is the best which has been suggested, if the following process be followed: Weigh out 0.7 gram of finely divided leather and place it in a 500 cc. round bottom Jena flask. Add 20 cc. concentrated sulphuric acid and by heating gently over a Teclu burner for 15 or 20 minutes, carbonize to a smooth black liquid, which should contain no small pieces of unattacked leather. Remove the burner and allow the flask to cool. The crucial point of the method is to choose exactly the right moment for the addition of the permanganate. If it is added too soon, while the contents of the flask are too hot, effervescence ensues, the oxygen escaping into the air. If it is added too late, the oxidation is too slow, and the contents of the flask must be again heated and the process repeated. In order to find the correct moment the following method is recommended: After the carbonized leather has been cooling about 5 minutes, add a very small crystal of permanganate. If it explodes or effervesces, wait a minute or two and add another. When no disturbance or only a slight one is observed on adding a small crystal, add a full pinch of permanganate, re-light the burner and heat strongly. The author uses a bare flame, twirling the flask. In this manner, in less than 2 minutes the liquid becomes perfectly clear and colorless and ready for distillation. The whole process when conducted in this way occupies not more than from ½ to ¾ hour. The author summarizes the essential points: (1) the material must be thoroughly carbonized, (2) the permanganate must be added at the right moment, (3) strong heat must be applied immediately after the addition. If the right moment is not chosen for the addition of the permanganate, the liquid will not come clear, and the operation must be repeated. The distillation is afterward carried out with excess of caustic soda, using a little zinc dust to prevent bumping, in the usual manner. Or the method of Ronchése may be followed, *i. e.*, titration of free acid after adding formaldehyde to the neutral liquid. The author finds the latter method unsatisfactory because of indistinct end-point.

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TWELFTH ANNUAL MEETING.

The twelfth annual meeting of the American Leather Chemists Association was held at Atlantic City, May 27, 28 and 29, 1915. The first session was called to order about 10 A. M., May 27 in a first-floor room of the Marlborough-Blenheim overlooking the boardwalk, President Louis E. Levi in the chair. His opening address is printed elsewhere in this number. Among those in attendance were the following:—Louis E. Levi, H. C. Reed, T. A. Faust, F. H. Small, W. H. Teas, W. A. Fox, R. W. Griffith, E. J. Haley, W. K. Alsop, Allen Rogers, J. S. Rogers, Charles Eachus, F. P. Veitch, Geo. D. McLaughlin, W. C. Carnell, W. H. Dickerson, Thomas Blackadder, Theodor Veit, C. C. Smoot, III, Oskar Riethof, B. S. Agnew, Sigmond Saxe, A. H. Lockwood, R. C. Jacobsen, Edward J. White, Roy J. Bailey, L. Balderston, William L. Alexander, N. A. Randall, Armand Daoust, Caspar Drueding, J. V. R. Evans, Cudworth Beye, F. O. Sprague, Clarence M. Allen, Robert Badcock, Ralph E. Porter, Reinhold A. Lang, C. M. Morrison, John Helfrich, H. H. Hurt, H. E. McCalip, W. L. Whitehouse, Roy H. Wisdom, L. E. Stacey, Jr., P. F. Reilly, J. M. Seltzer, F. S. Klebart, J. H. Barton, F. W. Kressman, W. H. Gardner, C. E. Heald, T. J. Mosser, A. C. Orthmann, Geo. F. Rumpf, Joseph J. Kelly, J. E. Rooney.

The first item of business was the report of the Secretary. This showed that 22 active members had been elected since last report, and 18 associate members. Five active members had resigned and one died, making a net gain of 16 in active members. Of associate members, 6 resigned and 2 died, net gain 10. The

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total number of active members May 1 was 160 and of associate members 152, grand total 312.

The Treasurer's report was then read by H. C. Reed. A summary of the report follows:—

TREASURER'S REPORT, 1914-1915—THE AMERICAN LEATHER CHEMISTS ASSOCIATION.

GENERAL ACCOUNT.

Receipts.		
Cash on hand Oct. 1, 1914		$ 846.96
Dues	$972.62	
Contingent expenses (returned)	99.00	
From Journal account	69.85	
Interest	8.22	1,149.69
		$1,996.65
Disbursements.		
Annual meeting expenses	$179.50	
Council meeting expenses	36.10	
Contingent expenses (part returned, as above)	100.00	
Secretary's expenses	166.68	
Committee expenses	35.88	
Printing, postage, envelopes, expressage and supplies	298.77	
Rebate on dues (paid twice)	5.00	$ 821.93
Balance on hand May 1, 1915		$1,174.72

JOURNAL ACCOUNT.

Receipts.		
From advertisers	$948.75	
From back numbers	3.50	
From bound volumes	59.85	
From subscriptions	45.00	$1,057.10
Disbursements.		
Journals (Oct., 1914, to April, 1915, inclusive)	$682.97	
Reprints	80.62	
Abstracts and translations	29.50	
Index	23.00	
Copywriting Journal	12.00	
Bound volumes	56.46	
Subscriptions to foreign journal	2.50	
Rebate on overpayment on advertisement	3.75	
Editor's expenses	97.35	$ 937.25
To General Account		$ 69.85

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SUMMARY.

Cash on hand Oct. 1, 1914		$ 846.96
Receipts, General Account	$1,079.84	
Receipts, Journal Account	1,057.10	2,136.94
		$2,983.90
Disbursements, General Account	$821.93	
Disbursements, Journal Account	987.25	$1,809.18
Cash on hand May 1, 1915		$1,174.72

Due from advertisers, dues and bound volumes—$933.05

F. H. Small and G. D. McLaughlin were appointed to audit the Treasurer's account.

John Helfrich next read his paper on "Chemical Control of the Beam-House," which will appear in the August JOURNAL.

The next item was the report of the Committee on Miscellaneous Methods by the chairman, L. Balderston. This report, which deals entirely with analysis of lactic acid, was printed in the May JOURNAL. The chairman prefaced his presentation of the report with a statement in regard to the Determination of Acid in Chrome Liquors. The accuracy of the Procter method, recommended in the report of the committee last year, had been called in question, and the suggestion made that the Alden method, (JOURNAL, vol I, p. 175), is more satisfactory. The chairman had compared the two methods and found them to agree very closely. A brief discussion followed the presentation of the report on Lactic Acid. Dr. Carnell suggested that the temperature at which the solution stands with excess alkali in determining anhydride should be specified. H. L. Feagley remarked that if the final titration for anhydride is made after boiling the solution with excess acid, the alkali should be standardized by boiling with excess acid and titrating back, because standard alkali solutions always contain some carbonate.

The next business was a paper by G. J. Laemmle on "Alum Loading in Raw Stocks," read by Dr. Allen Rogers, which is published in this issue.

T. A. Faust now presented his committee reports on Moellons and Hard Greases. The former report was published in the April and the latter in the May JOURNAL. An abstract of the discussion

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which followed will be published later in the JOURNAL. Adjournment to Friday morning followed.

The second session convened at about 10 o'clock Friday morning, May 28th. J. S. Rogers, chairman of the Committee on Determination of Free Sulphuric Acid in Leather, presented a verbal report, which was followed by an interesting discussion, in which Dr. Allen Rogers, H. C. Reed and others participated. This discussion will appear in a future number of the JOURNAL.

F. H. Small next presented his committee report on Filter Papers, which has since been published in the JOURNAL for June. A somewhat extended discussion followed, an abstract of which will be published later.

At this point E. J. Haley called attention to the fact that two members who have long been prominently identified with the work of the Association were absent on account of illness. He offered a motion that the Secretary be authorized to send the greetings and goodwill of the Association by telegraph to J. H. Yocum and C. W. Norris. The motion was unanimously adopted.

The next item of business was a paper by F. W. Kressman on "Osage Orange, a New Substitute for Fustic," which appears elsewhere in the current number.

L. Balderston now read a paper on "Extraction of Valonia," which will be published later.

A. C. Orthmann, chairman of the Committee on Tanning Materials in admixture next presented his report, which is published in this issue. T. A. Faust offered some additional facts on the epidemic of foot and mouth disease, an article on which by J. H. Yocum appeared in the May JOURNAL. Adjourned to 2:30 P. M.

The third session began with the reading by the secretary of a letter from C. R. Oberfell expressing his regret at being unable to be present. His committee report on Methods Connected with Beam-House Procedure published in the May JOURNAL was submitted for discussion, but no suggestions were offered.

F. P. Veitch was next called on for his committee report on Disposal of Tannery Waste. He presented a brief verbal report, and offered two papers; one by John Helfrich on "Recovery of Sludge from the Sulphide Unhairing Process," and one by J. M.

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Seltzer on "Sewage Disposal." Both papers are printed elsewhere in this issue.

F. O. Sprague now presented his report on "Extract Analysis, published in the May JOURNAL. A good deal of discussion on the relative merits of slow cooling and rapid cooling resulted. Many members expressed the opinion that one or the other ought to be dropped, but there was no agreement in regard to which one should be dropped. Further discussion was by motion referred to the closing session.

L. E. Stacey next read a paper on "Determination of Water Solubles in Leather," which appears in this issue.

F. H. Small read a note on the Alundum Thimble, which is printed elsewhere in this number, and showed a specimen of the improved thimble and rubber gasket.

J. H. Barton brought up the question of Determination of Neutral Fat in Sulphonated Oils. An abstract of the resulting discussion will appear later. Adjourned to Saturday morning.

Fourth session, Saturday, May 29, 10.30 A. M. The subject of Rapid and Slow Cooling in Extract Analysis came up from the preceding day. It appeared that no legal method of changing the method during the current year could be found, so the matter was left to take its regular course. On motion of W. H. Teas it was agreed that on reports of extract analyses it should be stated whether the rapid or slow cooling method had been used.

The election for two members of council resulted in the choice of F. H. Small and T. A. Faust.

President Levi now announced the death of three members during the year, and voiced the sorrow of the Association. These were R. Arnold Seymour-Jones, S. F. McDonald and Charles S. Forsyth.

Cudworth Beye, executive secretary of the National Association of Tanners called attention to the fact that the spring meeting of that Association will be held in Newark, N. J. in April 1916, and expressed a hope that the A. L. C. A. meeting would be held at the same time and place. Then adjourned.

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COUNCIL MEETING.

Immediately after the adjournment of the convention, the new Council met. President Levi introduced Cudworth Beye, who said that the Quarantine Division of the Bureau of Animal Industry at Washington were proposing an amendment to their hide disinfection circular, and had asked the Association for suggestions. J. H. Yocum had been consulted, and the Bureau had not been entirely satisfied with his suggestions, so the matter was still undecided. A report by F. W. Stilley was published April 15, telling of recent experiments at Washington on different methods of disinfection. F. P. Veitch has offered to conduct experiments on a practical scale. Mr. Beye suggested that the Council appoint a committee on the subject, to include J. H. Yocum and F. P. Veitch.

Five active and ten associate members were elected.

It was decided to hold the next council meeting at the Chemists Club, 50 E. 41st St., New York, on July 2, at 2 o'clock.

NOTES FROM TANNING COURSES AT PRATT INSTITUTE.

On Tuesday, May 25th, the third quarterly meeting of the Joint Advisory Committee of the National Association of Tanners and the American Leather Chemists' Association was held at Tanners' Institute, Messrs. George H. Raymond, chairman, Morris S. Barnet, Wm. H. Healy, H. C. Reed, Wm. H. Teas and Cudworth Beye being present. In the morning the committee thoroughly examined the work of the tanning courses in the class room, attending recitations in chemistry, leather manufacture, and tannery design. An inspection of the entire school was then made. At noon a very excellent lunch was served by the household science and arts department. After luncheon the committee held a round-table discussion of the curriculum of the tanning courses. The committee were invited to criticize the make-up of the courses, and they expressed themselves satisfied with what they had seen of the work of the students.

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PRESIDENT'S ADDRESS.*

By Dr. Louis E. Levi.

It is customary, I believe, for the President to open the convention with an address of welcome to all members and guests of the Association, to invite them to take part in the program by reading papers and to participate in the discussion which naturally follows the presentation of subjects of interest to those banded together by the common tie—"Science." The papers will undoubtedly be of great interest to all of us, presenting entirely new fields of research as well as improvements in the fields of leather chemistry which have been given to the world in years gone by. All this work represents a great deal of time and labor spent by the members of this Association in their chosen profession, and should be highly appreciated, not only by us but also by the layman, for whom this work is of special benefit.

Among the subjects which are naturally foremost in the minds of all is the JOURNAL of our Association. The editor has a very hard task before him to give to the members every month a JOURNAL, the pages of which shall be filled with articles written by members. Instead of articles we most desire, we find theses written by non-members, although very fine and meritorious, yet the JOURNAL was founded to be a clearing house for American thought and science, and at the same time to keep us in touch with the mental activities of the master minds of foreign countries. Surely the American Leather Chemist can devote 10 per cent. of his time to original research and write an article for the JOURNAL, which will be of such high value to bring honor upon himself, and by its reflection illuminate the pages of the JOURNAL to make it a thing of beauty and a joy forever. I have just spoken about the chemist as a member, but we are fortunate in having a large number of associates who have been trained in the practical school of tanning and science and also in the science of salesmanship, whose articles would be of inestimable value. In reading the JOURNALS month by month, we fail to find the thoughts and experiences of those associates we so much desire. Articles written by the practical man and salesman tend to leaven the

* A. L. C. A. 12th annual meeting, Atlantic City, May 27, 1915.

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dough of science and teach us to know how things are, for the chemist knows how things ought to be. Without the practical man to stand back of us and keep the train of chemical thought upon the rails, the chemist quite often would be wrecked by the log of theory laid upon the track. The salesman, whose wide experience in meeting men of all nations, is also most ably fitted to prepare most valuable dissertations upon subjects which the chemist does not know and would appreciate highly.

Now, gentlemen, I want to impress upon you the necessity of giving to the JOURNAL the benefit of your thoughts by writing papers, thereby raising our publication to that pinacle where the siege gun of foreign men of science cannot dislodge the man behind the gun in the fortress of American brains. To keep abreast with the times and take up topics of the day, especially those which are of greatest interest to the Association, I crave your attention for a few minutes longer, for as brevity is the soul of wit, I will occupy your attention and will say but very few words about the need of a first-class research laboratory. In looking into the advancement of tanning, one naturally comes back to those countries whose advancement is most marked. The strides made are such as to make one "Stop, Look and Listen." In analyzing the situation, we come to the conclusion that those countries in which the most progress has been made, the research laboratory, where picked scientists and practical experts are employed, are the ones where the tanning industry has forged ahead beyond all conception. We are now facing a proposition by which the United States, the birth-place of Chrome Tanning, is to take its place among the progressive nations of the world. This place should never have been taken away from us but for the "show me" policy of the American, which has always been wrongly applied. From this condition our country is now rapidly recovering and the American tanner is now awakening from his Rip Van Winkle sleep and concedes to the scientist his worth. The Association of American Leather Chemists should as a body and individually stand back of the tanner in this vital cause, giving him the necessary advice and hearty support. The question will come up as to the amount of money necessary to launch this project and should be dealt with in sober and hard thought, so

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as not to kill the goose that lays the golden egg. The next question of importance will be the scientist to employ for the directorship of the laboratory. There are a great many very able men to be had for the directorship, but one should always profit by the doings of others, and not go out from this land of possibilities, for there are just as able and scientific men in our own country as in any country of the world, men, who when given the chance and money to carry on the great work of research, which is now in contemplation, will startle the world of tanners by the epoch making discoveries, and the United States will again come into its own. The place where the laboratory should be situated when the necessary funds have been voted, is of great importance and should be so centrally located as to be of easy access to the greatest number of tanners and chemists. When the urgent need of a research laboratory has been filled and the work turned out by the institution is of such great value to the tanner, he will think of the poet Sheridan and change his immortal saying a trifle to suit the occasion, and send to the research laboratory this motto:

"He who tans and tans our way, lives to tan another day."

Not only does science call us together once every year for conference but that desire to place in the shaker of activity a substance which will combine easily with the most common element known to chemistry, namely "work," and by its union with this element form a compound, the fundamental product, whose benefit to the hard worked chemist is many fold, namely "relaxation." Work and relaxation when brought into juxtaposition gives to us those chemical compounds which Ponce de Leon so ardently tried to find, "Pleasure and good-fellowship," the source of the fountain of youth. With pleasure and good-fellowship working side by side with science, those hours spent in hard and strenuous labor will be lightened by the thought of our next annual meeting, when we hope to meet again to enjoy each others society.

Gentlemen, I welcome you.

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OSAGE ORANGE, A NEW SUBSTITUTE FOR FUSTIC.*

By F. W. Kressmann.

Chemist in Forest Products, Forest Products Laboratory, Madison, Wis.

The study of osage orange as a dyewood was begun by the United States Forest Service at the Forest Products Laboratory about three years ago and was the result of an investigation on the utilization of osage orange mill waste. Last year an article was published in the *Textile Colorist* and in the *Journal of Industrial and Engineering Chemistry* in which osage orange and fustic were compared from a textile standpoint. The newspaper notoriety and publicity given this work some weeks ago is the result of a visit of a newspaper man at our laboratory. He presented an exaggerated statement to the press, probably because of the "human interest in it" and the agitation it would arouse in view of the war and the present shortage of aniline colors.

Although osage orange seems to have been used in a desultory manner in Texas as a dyewood for many years, especially years ago by the Indians in the Red River Valley region, it does not appear to have been compared with fustic, which it resembles very closely from a dye standpoint, until within the last few years, and the above publications apparently were the first to report this. I wish to take a few moments to review the above work and to show you a series of mordanted wool yarns, each set being dyed with the same amounts of each of the dyewoods in identically the same way. As you will see, the colors are very similar, the osage orange colors being slightly purer and not quite as red as the fustic.

This is especially true when comparing with the Tehuantepec fustic which contains a considerable amount of red. The Jamaica fustic is not as red as the Tehuantepec fustic which even shows itself in the wood, as these samples that I have here indicate. The Jamaica and Maracaibo fustics are used for blending with Tehuantepec fustic. The color cards show the Tehuantepec material compared with osage orange and the different mordants

* Read at the Twelfth Annual Meeting of the American Leather Chemist Association, Atlantic City, N. J., May 28, 1915.

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used and in addition Jamaica fustic with the tin and chromium mordants.

A qualitative study of the aqueous extract obtained from the osage orange wood showed that the dyeing principles present were, as in fustic, morin or moric acid and morin tannic acid or maclurin, but that the unknown red constituent present in variable amounts in fustic from different localities was practically absent in the osage orange.

We next secured the interest of a number of textile schools in the country, among which were the Philadelphia Textile School, New Bedford Textile School, Lowell Textile School, the North Carolina College of Agriculture and Mechanic Arts, and the Georgia School of Technology. Samples of the wood in the form of shavings and sawdust were submitted to these institutions for comparison with fustic. Their reports may be summarized as follows:

1. The character of the dyeing produced is almost identical with that of fustic, each being a polygenetic mordant dyestuff.

2. Opinions differed as to the depth of the colors produced: Some believe the osage to give a deeper color to a given weight of wool than fustic and others believe the osage orange to be only 75 to 80 per cent. as strong as the fustic. The difference is apparently due to differences in the fustic that was used for it is the opinion of men in the trade that the Tehuantepec fustic is a better article than either the Jamaica or Maracaibo material.

3. In regard to fastness to light, weather, washing, etc., all of the opinions were concurrent in that the aluminum and tin mordanted colors produced by osage orange as well as fustic were too fugitive to be of commercial value. The copper, chromium and iron mordanted colors, however, were all of commercial value, the chromium being especially resistant to light and washing. No differences could be noted between the osage orange and fustic colors in any of the fastness tests.

4. Opinions differed as to the amount of water soluble colors in the osage orange, due probably to the different methods of extraction which were used. Our own results are as follows:

	Moisture per cent.	Water soluble extract Dry basis per cent.
Texas osage orange	10.90	14.90
Tehuantepec fustic	7.60	17.77

In view of the striking similarity of these two materials, from a textile standpoint, it was not unreasonable to expect that osage

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orange should be as valuable for leather dyeing purposes as fustic and this seems indeed to be the case.

While in Milwaukee several months ago, in a discussion of other matters, I mentioned some of the results we had obtained with this material on wool yarns to your worthy president, Dr. L. E. Levi. He became quite interested in the possibilities of the material from the tanners' standpoint and desired to test it out as a leather dye, and, after having done so, felt that the results were of sufficient value to be brought before you so as to acquaint the leather chemists of the country with the possibilities and value of this material. The results of this work, therefore, and the sample I will show and present to you are all the result of Dr. Levi's suggestion and endeavors, and I wish to take this opportunity for thanking him for his kindness and cooperation and to the Pfister and Vogel Leather Company for having made the results a permanent record in the form of these small samples of osage orange and fustic dyed, chrome tanned calf, which I will pass around and of which I hope you will each accept one A bag of osage orange shavings which was part of a shipment obtained from a Fort Worth, Tex., wagon manufacturing company, was sent to Dr. Levi for these tests.

Fifteen pounds of the shavings were leached with 25 gallons of hot water and the 24 gallons of dilute extract obtained were concentrated under a vacuum to ½ gallon of extract having a specific gravity of 1.125 at 23° C. A commercial fustic extract obtained from a well known dyewood extract manufacturing company having a specific gravity of 1.258 at 23° C. was used for comparative purposes. The two large calf skins and the two sets of small samples which were cut from two others were dyed with the above extracts; in each case 5 per cent. of the drained tanned weight of chrome calf was used. As you will note, the osage orange is a little brighter and purer than the fustic, even though the extract used was much lower in gravity than that of the fustic. Using extracts of equal gravity, the osage orange would undoubtedly have produced a color considerably deeper than the fustic. It appears then that osage orange for leather purposes, as well as textile work, can replace fustic wherever the latter is being used.

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A domestic material, therefore, has been found which seems to be able to replace a foreign material in all its different fields. Moreover, we have a domestic material which is not and has not been subject to the difficulties involved in the cutting and transportation of a tropical exotic wood whose source and place of production has been a place of revolution and strife as in Mexico.

A representative of the Forest Products Laboratory has been in Texas and Oklahoma within the last few weeks looking up the osage orange in that region where it is most abundant. Wood from this region was the wood used for these tests and, although one test has been made from northern grown stuff from Indiana, the latter does not appear to contain the dyes in commercial quantities. From the information that the laboratory has gathered on this subject, it appears that at present from 40,000 to 50,000 tons of Texas and Oklahoma material are available annually, which is more than double the present fustic consumption; also that good osage orange can be obtained in Texas and Oklahoma for from $4.50 to $6 per ton. This material can be shipped within the state of Texas at 8 cents per hundred, making the rate to Galveston $1.60 per ton. From Oklahoma points to Galveston the rate varies from 12 cents to 18 cents per hundred. Excellent storage and wharf facilities are available at Galveston and the material can be brought North to our northern Atlantic ports by schooner at from $3 to $5 per ton. So that even without the present artificial stimulus of the war which has boosted the price of fustic to more than double its normal price, it should be possible to have osage orange at from $10 to $14 per ton f. o. b. our ports compete to advantage with foreign fustic at $18 or $20, which was the price f. o. b. our Atlantic ports before the war.

Our laboratory at present is in touch with a large number of producers in the Southwest, some of whom have large quantities of waste on hand which, no doubt, would be available at an attractive figure. One of the difficulties has been to get the dyewood extract manufacturers interested sufficiently to take hold and push the work. Being naturally conservative, they could hardly be expected to do this unless an active demand for the product exists. A number of them have tried out osage orange

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and admit its merits and one of the reasons for my being here to-day is to acquaint you with its possibilities and results so that you, as one of the consumers of fustic, may know of the existence of this material, its value, and also that it has a definite place in constructive conservation in the Southwest of our own country.

"ALUM LOADING" IN RAW STOCK.*

By George J. Laemmle.

All of the problems of the tanner and the chemist are really expressed under the old heading of "Gains." The constant factor is the weight of the raw stock. We have been taking it for granted more or less that this weight of the raw stock is a constant factor but I wish to say that a practice of loading to create false weights is becoming rather general and unless organizations like the American Leather Chemists' Association and the National Tanners' Association take a decided stand very soon on this question, loading will in time become an accepted feature in the leather business. When that time arrives it will be found very difficult if not impossible to buy raw stock in proper condition.

It is the proper function of the tanner's agent who is sent out to "pick up" hides or skins, which have already been bought, to see that they are received in proper "condition." When the skins or hides are pulled out of the bed and banked overnight for the receiver both parties to the contract are generally satisfied with the "condition." In some cases, a further allowance is made for loss of weight during transit. Where the tanner has been buying lots of raw stock from the same dealer over a number of years, the final reports of measurement and substance will eventually reveal any large variations in the condition of the raw stock. While it is a poor enough system at best of judging the amount of water it would be tolerable if left there.

In past years there have been rumors regarding some few hide dealers and after several experiences with such a dealer, the

* Read at the Twelfth Annual Meeting of the A. L. C. A., Atlantic City, May 27, 1915.

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tanner would cut him off the list, but the information was bought at a big price. "I don't know what's the matter with that fellow's skins," says the tanner. "His weights are all right and the skins look all right but I can't 'come out' on his shipments." This means that the measurement and substance reports did not correspond to the weights. And generally the discrepancy is a large one before the tanning superintendent is exonerated and the fault placed where it properly belongs, with the hide dealer.

Where the practice was confined to a few unscrupulous dealers it was well enough to avoid them and let it go at that, but I am finding from day to day that this loading is extending to the prominent shippers in whom the tanners place full confidence. A few months ago I tested about fifteen successive lots and found alum in eight of them and all of the shippers were big dealers.

The material most used for this purpose is sulphate of alumina and is referred to as "alum" in the trade although this is a misnomer. It crystallizes with difficulty retaining eighteen waters of crystallization. Approximately, this means that every pound of "alum" retained by the raw stock, itself retains a pound of water. A pickle is usually made and the alum dissolved in the pickle. The hides or skins are then dipped in this pickle and then resalted. The method of loading varies considerably with each cellar but this is probably the general method.

My experience has been wholly obtained on calfskins but I dare say that a study of hides would reveal the same facts. Calfskins loaded with this material have a greasy appearance on the hair side but there is no odor. In good light the hair will appear sleek but hide cellars are not usually provided with good light. If the condition is suspected and the skins are banked overnight they will not lose weight. Tests which I have made, keeping the skins banked for 48 hours, showed slight gains rather than the losses which I expected. The flesh side gives no indication.

As sulphate of alumina costs for the best qualities only 1¾ cents per pound, the dealer is not put to much expense in bringing up his weights. The difference in weights is a large enough factor to merit the immediate and full investigation of all tanners and chemists. The raw stock weight on an honest basis is a poor enough "constant factor" in computing tannery gains but

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in my opinion the chemist's efforts to economize on tan and other raw materials in the tannery resemble "a saving at the spigot and letting it run out at the bunghole" when alum loading is passed by. I am sure you will find on investigating this point that chemical control will have to begin in the hide cellar instead of the soaks. The gain in weight obtained by alum loading whittles away a considerable portion of the tanner's profit, if not all of it and the practice has extended so that it is now impossible to avoid such loading by simply keeping away from certain dealers. Alum loading is purely an adulteration and its use cannot be defended from the standpoint of assisting in the cure or prevention of salt stains.

Chemists will recall that sulphate of alumina replaced the true alums in alum tannage only when the manufacturers were able to sell it "iron free." The separation of iron in commercial sulphate of alumina was not easily accomplished and is to-day confined to the best grades. We can imagine that the hide dealers who use this method of loading are not so insistent as the tanners in demanding an iron free product even at greater cost, and we will probably find a percentage of "salt stain" stock in such lots.

In alum loading we have also to consider the use of sodium carbonate. In the resalting, a small percentage of sodium carbonate will make a basic sulphate of alumina which as a loading material could scarcely be improved. Chemists, knowing the gelatinous character of the basic salt, will fully appreciate its ability to retain not only water but dirt, particles of manure, etc. Also, that when imbedded in the hair, because of its lack of odor and color, only a chemical test will prove its presence.

In this connection, we must remember that sulphate of alumina is readily made basic without the use of sodium carbonate. Hide substance itself will do it. Ammonia fumes will do it as well and these exist plentifully in a hide cellar due to manure, decomposition, etc., particularly where hairslip skins occur in the pack.

As the sulphate is made basic under these conditions free sulphuric acid is given off but the presence of salt prevents the swelling that would ordinarily occur. The brief soaking that skins receive and the well known affinity of hide substance for sulphuric acid would make it possible for the skins to retain a

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portion of it up to the point of entering the limes. Hence, calcium sulphate would be formed, which aside from the small waste of lime which we can ignore, is with difficulty washed out, becoming still more fixed in the pickles and seriously interfering with the character of the leather. Where hard water is used in the soaking we can expect the calcium sulphate to be fixed in the skins before they are entered in limes. Some months ago a New England tanner told me that these unscrupulous hide dealers were now using sulphuric acid, to plump the hides and increase the weight. I suspected at the time that the sulphate test was obtained because of alum loading.

I am now leaving the mere question of weights and considering the effects of alum loading from the tanning standpoint as it affects the quality of leather. Therefore, I consider the remaining product of hydrolysis, aluminum hydroxide, more to be feared. By the time the skins enter the soaks I believe that any sulphate of alumina originally used in loading has been changed by the hide substance to a basic salt, if not to the hydroxide and where soft water is used for soaking we can expect incomplete leaching, if it is not more firmly fixed. On entering the limes the precipitation is fully completed. At this stage the skins are by no means ready for a tannage and it is probable that drawn grain in the soft parts of the skin, *i. e.*, the belly, are due to this precipitation of alum in the limes. This alum may be removed in the pickles but I believe that the evidence would remain in the grain.

I have no definite proof to offer as yet that such results are obtained in the tannage when alum loading is practiced but they are natural assumptions that a chemist would make and follow out, particularly when occasional lots come through the tannery with grain in the belly. If the process itself puts the grain there, then we would notice it on all lots or at least a good percentage but when this grain appears in about the same ratio that the hide cellar tests show alum, then we have fair ground for the assumption and enough temptation to devote considerable time to the proving of it.

There are many variations to the practice but these will all come out if the Association takes this matter up vigorously, as I hope

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it will. I will mention just one instance which came to my notice a few weeks ago.

Some few months ago, to go back a little, I picked up a lot of about 11,000 skins from one of the largest dealers. His skins were always considered "prime" stock. The skins had always come to the tannery in clean, good condition and the final records always showed a constancy of measurement and substance until about a year ago when the measurement fell off although the weights held up. Having picked up the last three or four lots personally with this falling off in measurement constantly in mind I was at a loss to understand the falling off. Though it was high treason to associate alum loading with such a dealer, in such a market, I tested the skins but found no alum loading. On this lot of 11,000 that I mention, I was suddenly confronted with another new fact at the tannery, that they showed about 12 per cent. salt stain. This was unbelievable because we knew that the dealer used "salt stain powder." I had never looked into this phase of it. One reason, it had not occurred before; another, the skins were clean and fresh and I knew of the powder being used and assumed that it was the salt stain powder that we all have tried.

So on this last trip of a few weeks ago I did some investigating in that hide cellar and although I can't say I located the whole stock, I located 15 barrels each containing 305 pounds of pure anhydrous sodium carbonate. I quizzed everybody in sight, from managers down to the workers in the cellars, naturally throwing out leads which covered my real purpose and secured absolute proof that this was the "salt stain" powder they were using. They were also using Liverpool salt. I looked into Liverpool salt sometime ago to find out why it was more popular with American hide dealers than New York salt. It has no alum or iron, at least the samples I had gave no test, but it contained calcium chloride. Experienced workers in hide cellars have told me again and again that they like Liverpool salt because "it keeps the stock damp" whereas New York salt makes it too dry. Chemists will readily understand this property from the hygroscopic character of calcium chloride.

I remember also that in one of the reports from the English

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Section of the I. L. C. A. someone has suggested, rather faintly I thought, that sodium carbonate in conjunction with salt was a good preservative and a preventative of salt stain. I can't see it that way. If anything, the sodium carbonate would fix the iron as the hydroxide and I consider that when we get 12 per cent. salt stain in a lot of fresh city skins where sodium carbonate has been used that this disposes of sodium carbonate for salt stain for all time.

In few of these facts, I concluded that the powder was not used to prevent salt stain; that it worked the other way. I figured that the powder was used purely as a weighting proposition. The anhydrous salt absorbs ten waters of crystallization, hence its value. Furthermore, it is a fine white powder which lends itself ready to mixing and uniform spreading.

In conjunction with the calcium chloride of the Liverpool salt it will form calcium carbonate so we have a fine chemical combination. We have a hygroscopic salt present which attracts moisture to the skin and we have one of the best agents obtainable, anhydrous sodium carbonate for retaining that moisture and we have two chemicals present which will form insoluble calcium carbonate. I now believe I have located the reasons for salt stain and falling off in measurement in skins from that particular dealer. Needless to say, I took samples of the "powder" and of the Liverpool salt and also of the mixed salts in the barrels on the various beds and these confirmed in the laboratory tests all that I ascertained in the cellar. Also, armed with this information, I threw out all line and light skins with reckless abandon so that I know I am covered on my weights. When the skins arrived in the tannery I tried phenolpthalein on them to see if I would get the test I expected but I didn't get it. I cut off a shank and tried to get the test in solution but it failed there so I have concluded that while in transit all of the alkali had gone over to calcium carbonate. Now aside from the weighting, these propositions always involve the tannage. Tanners avoid exposing limed stock to the air as much as possible to avoid "Lime Blast" or the forming of calcium carbonate. But the dealer now helps matters along by forming "Lime Blast" for us before we put the stock in the soaks.

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There are then two features to be considered in "alum loading" or any other kind of loading; the false weights which limit the chances of profit on such lots, and the injurious effect of the loading material on the skins from the tanning view.

I do not believe that any single tanner can make any headway against this practice as it is becoming too general. The American Leather Chemist's Association is the proper organization to take up the crusade, backed up vigorously by the Tanners' Association. What penalties and what official tests shall be worked out will be revealed quickly enough in the discussions in the JOURNAL, which I hope this paper will start.

For the benefit of the selector on the road who might come across such a lot, I might mention that the skins will have the appearance of poor condition, but will not lose weight on banking. The selector's hands will whiten and pucker after handling a few hundred, and this will be more noticeable when the hands dry. When skins are pickled in the ordinary way and seem in poor condition, selectors generally run the knife edge with the hair down to the end of the shank. When the knife is released the pickle will fall into the hair quickly, but when alum is used it will stay where the knife stopped, like mud. Another sign is that the hair feels greasy to the hand but has no odor.

In the laboratory, leaching with hydrochloric acid and then precipitating with ammonium hydroxide gives the alum while the filtrate is tested for the sulphate radical by addition of barium chloride.

Regarding foreign salts which are denatured for commercial purposes such small percentages as are demanded by foreign governments would never yield the tests I have secured on foreign skins. Usually a list of denaturing agents is submitted by the governments and it is not difficult to see why alum would be chosen by hide dealers, but even here it seems to me that the A. L. C. A. and the Tanners' Association could insist upon the selection of some other harmless denaturing agent, not because of the action of the small percentage used for denaturing, as for the latitude it allows for wider adulteration.

Barnet Leather Co.,
Little Falls, N. Y.

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DISCUSSION.

Mr. Helfrich remarked that the loading of raw stock is not confined to green salted stock. He had known a bale of dry calfskins to lose 22 pounds in weight after being in the warehouse one week. When the bale was received and examined, skins were found in the middle of the bale that were just as wet as if they had been in soak for three days and then drained.

L. Balderston called attention to the statement in the paper (top of page 35) that calcium sulphate is with difficulty washed out of the skins and becomes still more fixed in the pickles. The author seemed to have assumed that because calcium sulphate is insoluble in water it would become fixed in the skins, but did not mention any experiments proving its presence. The speaker had occasion to try some experiments on sulphuric acid baths for plumping heavy hides for sole leather. He had always supposed that if at this stage calcium sulphate was formed in the hide, much of it would remain there through the subsequent processes. Pieces of hide from the limes were drummed in a bark liquor for a short time to color them, and then soaked in dilute sulphuric acid of various strengths for varying times and then tanned. The lime in the hide was determined at each stage of the process. It was found that a piece of heavy limed hide immersed for 24 hours in an acid bath of suitable strength for plumping was at the end of the time almost free from lime, and the lime was formed in the acid solution. In view of these results the speaker thought that calcium sulphate would be more likely to be washed out of calfskins that fixed in them by pickling.

Mr. Helfrich said that sulphuric acid will take the lime out of a calfskin. He had never found much calcium sulphate in a pickled calfskin.

T. A. Faust said that Mr. Yocum had tried experiments in this line some years ago, and found that very little calcium sulphate remained in the later stages of tanning.

H. H. Hurt said that the removal of calcium sulphate was explained by the fact that calcium sulphate is more readily soluble in the acid liquors used than in pure water.

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REPORT OF THE COMMITTEE ON THE DETERMINATION AND ESTIMATION OF TANNING MATERIALS IN ADMIXTURE.

By August C. Orthmann, Chairman.

The following letter and instructions were sent to the various members of the Committee:

Letter.

The amount of work the subject of "Determination and Estimation of Tanning Materials in Admixture" covers is unestimatable and on looking up the literature regarding the same the Chairman finds that there is no method that will determine separately any of the true tannins if in admixture with other true tannins. As there are substances on the market that will make leather but without all the properties of true tannin and which cannot be defined as true tannin as generally known to chemists and yet cannot be condemned on account of the fact that they possess the property of rendering hide in putrescible, I thought it essential to work on a method that would separate the true tannin from the above mentioned, this comes under the scope of the title of this Committee.

As the time for doing any amount of work on this subject is rather limited I chose the above on account of having considerable data on hand but which data needs substantial collaboration.

Accordingly I am sending you under separate cover 3 samples of extracts and one bottle of Reagent No. 33 which you will kindly analyze according to the enclosed method of procedure.

The samples of extracts are mixtures of true tannin with sulphite-cellulose extract. No. 2 being a sample of ordinary quebracho.

You will find the published work on this subject in the J. A. L. C. A. of October, 1911, January, 1913, April and August, 1913.

Instructions.

Method of Analysis.—Make analyses of the extracts Nos. 1, 2, and 3 by the official A. L. C. A. method for tannin analysis, using about 12½ grams of the extract per liter of water. Re-

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serve about 100 cc. of the soluble solids solution for the following method:

Determination of True Tannin.—Take 10 cc. of the soluble solids, place into a 50 cc. beaker, 10 cc. of the reagent No. 33 are added from a burette and thoroughly mixed, the beaker being covered with a watch glass and allowed to stand over night (at least 12 hours), then filter through an 11-centimeter folded filter into a 300 cc. Florence flask, wash the precipitate with distilled water at room temperature until free from the reagent, which requires about 100 cc. of water. Discard the precipitate and determine cubic centimeters "hypo" titration of the filtrate in the following manner:

To the contents of the flask add about 5 grams of C. P. sodium peroxide, shaking the flask well, then boil until all free oxygen has been driven off which requires about one half to one hour. Then dilute to about 150 cc. and cool to about 15° C. When cool slowly add an excess of cold dilute sulphuric acid, cool again and add 1 gram of potassium iodide in solution and immediately titrate with N/10 sodium hyposulphite solution using starch as indicator. This is the usual iodometric method for the determination of chromates. This titration gives the number of cubic centimeters of "hypo" for the reagent remaining after precipitation of the tannin, titration "B." At the same time determine the number cubic centimeters of "hypo" required for 10 cc. of the reagent, by oxidizing with sodium peroxide and carrying through in the same manner, titration "A."

The difference between titrations "A" and "B" is multiplied by the factor 0.00574317 × 100 and divided by the amount of material taken to obtain the per cent. of pure tannin. (See J. A. L. C. A. for August, 1913, page 311.)

The Chairman finds that 10 cc. of the reagent No. 33 requires about 37.0 cc. of N/10 "hypo" solution.

Make all analyses in duplicate and report the full results of the hide powder method and by the method using reagent No. 33.

The following extracts were used to make up mixtures for the committee work.

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Sulphite-cellulose.
Ordinary quebracho.
Chestnut.

Analyses follow. Analyses made by Chairman, average of duplicate analyses.

	Sulphite-cellulose Per cent.	Ordinary quebracho Per cent.	Chestnut Per cent.
Total solids	48.85	42.76	45.23
Soluble solids	46.10	39.26	44.46
Non-tannins	20.56	4.26	17.02
Insolubles	2.75	3.50	0.77
Absorbed by hide powder	25.54	35.00	27.44
Tannin by reagent No. 33	4.23	35.08	25.33

The following samples were made up and sent to members of the committee:

Sample No. 1 consisted of—
300 parts sulphite-cellulose
700 parts ordinary quebracho

Sample No. 2 consisted of—
ordinary quebracho

Sample No. 3 consisted of—
300 parts sulphite-cellulose
700 parts chestnut extract.

ANALYSES OF SAMPLE NO. 1 BY COMMITTEE MEMBERS.
Results are Averages of Two Analyses.

	Balderston Per cent.	Faust Per cent.	Wisdom Per cent.	Orthmann Per cent.
Total solids	42.42 44.41*	43.85	43.83	44.67
Soluble solids	38.00	38.52	38.56	38.94
Non-tannins	7.15	6.55	7.18	7.91
Insolubles	4.42 6.41*	5.33	5.27	5.73
Absorbed by hide powder	30.85	31.97	31.38	31.03
Tannin by reagent No. 33	26.02	25.24	27.11	24.05

	High Per cent.	Low Per cent.	Difference Per cent.	Average Per cent.	Calculated Per cent.
Total solids	44.67	42.42	2.25	43.84	44.59
Soluble solids	38.94	38.00	0.94	38.51	41.31
Non-tannins	7.91	6.55	1.36	7.20	9.15
Insolubles	6.41	4.42	1.99	5.33	3.27
Absorbed by hide powder	31.97	30.85	1.12	31.31	32.16
Tannin by reagent No. 33	27.11	24.05	3.06	25.61	25.83

* Measured out in a graduated cylinder.

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ANALYSES OF SAMPLE NO. 2 BY COMMITTEE MEMBERS.
Results are Averages of Two Analyses.

	Balderston Per cent.	Faust Per cent.	Wisdom Per cent.	Orthmann Per cent.
Total solids	42.13	42.07	42.04	42.76
Soluble solids	39.50	39.35	39.62	39.26
Non-tannins	3.28	2.96	3.26	4.26
Insolubles	2.63	2.72	2.42	3.50
Absorbed by hide powder	36.22	36.39	36.36	35.00
Tannin by reagent No. 33	37.85	37.24	34.00	35.08

	High Per cent.	Low Per cent.	Difference Per cent.	Average Per cent.
Total solids	42.76	42.04	0.73	42.25
Soluble solids	39.62	39.26	0.36	39.43
Non-tannins	4.26	2.96	1.30	3.44
Insolubles	3.50	2.42	1.08	2.82
Absorbed by hide powder	36.39	35.00	1.39	35.99
Tannin by reagent No. 33	37.85	34.00	3.85	36.04

ANALYSES OF SAMPLE NO. 3 BY COMMITTEE MEMBERS.
Results are Averages of Two Analyses.

	Balderston Per cent.	Faust Per cent.	Wisdom Per cent.	Orthmann Per cent.
Total solids	45.88	45.62	45.90	46.56
Soluble solids	43.08	42.94	44.41	44.18
Non-tannins	15.79	14.72	18.03	19.49
Insolubles	2.80	2.68	1.49	2.38
Absorbed by hide powder	27.29	28.22	26.38	24.69
Tannin by reagent No. 33	17.34	19.10	13.32	17.17

	High Per cent.	Low Per cent.	Difference Per cent.	Average Per cent.	Calculated Per cent.
Total solids	46.56	45.62	0.94	45.99	46.32
Soluble solids	44.41	42.94	1.47	43.65	44.95
Non-tannins	19.49	14.72	4.77	17.01	18.08
Insolubles	2.80	1.49	1.31	2.34	1.37
Absorbed by hide powder	28.22	24.69	3.53	26.64	26.87
Tannin by reagent No. 33	19.10	13.32	5.78	16.73	18.93

CUBIC CENTIMETERS N/10 "HYPO" REQUIRED FOR 10 CC. OF REAGENT NO. 33.

Balderston	37.8 cc.
Faust	38.0 cc.
Wisdom	36.9 cc.
Orthmann	37.2 cc.

CRITICISM.

BALDERSTON: None.

FAUST: None.

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WISDOM: Believes that in commercial mixtures of fairly large percentages the method is applicable, in small amounts and especially in mixtures which form insolubles, the information may be misleading and prefers the Procter-Hirsch test in such cases.

CHAIRMAN: It is my opinion that the method can be used for the purpose of quantitative determination of pure tannin in mixtures of same with the so-called "tannins" that are not chemically known tannins.

The discrepancies shown by the results of the members of this committee I believe are due to an error in the determination of the chromium in the reagent and not in the precipitation of the true tannins by the reagent, in other words the precipitation is quantitative.

As a basis for this statement attention is directed to the different results obtained by the different operators on the titration "A" of reagent No. 33, the biggest difference being 1.1 cc. N/10 "hypo." The samples of reagent No. 33 being all the same, taken out of the stock solution the writer had on hand.

I would suggest that the work be carried on on a larger scale with different mixtures and urge for a committee of larger membership.

DETERMINATION OF WATER SOLUBLES IN LEATHER.*

By C. C. Smoot, III and L. E. Stacey.

In determining the water solubles in leather there are four factors to be considered—method of sampling, preparation of sample, temperature and time of extraction—assuming all extractions are made on the basis of two liters for 30 grams of leather. This paper only deals with the last two factors—temperature and time.

In order to control the temperature and time of extraction, we have designed an apparatus with the following general outlines. Three copper tanks supported by an iron stand are superimposed upon each other. The top tank is a receptacle for distilled water used as the solvent. It is block tin lined and connected to block tin coils which pass into the tank immediately below, termining

* Read at the Atlantic City Meeting, May 28, 1915.

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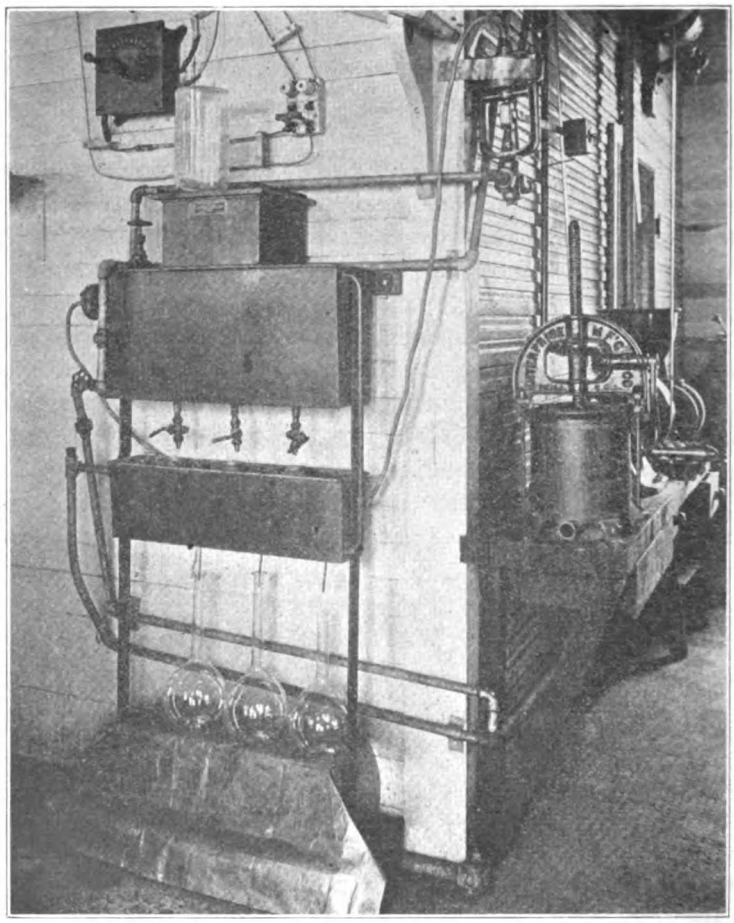
into pet-cocks for regulation of flow of solvent. The second tank is the temperature regulator. It is about 12 inches deep with a water connection, and steam coil in bottom. This tank also con-



tains thermostat control element for steam inlet. By regulating the flow of water the third tank which contains copper soxlets in which the extraction takes place is heated by the overflow from tank two. It has been found that this temperature can be controlled within limits of 2° C.

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The copper soxlets which are in the bottom tank are cone shape so that the alundum thimbles fit smugly in bottom. They are 7 inches tall which allows the use of a 6-inch thimble. The distance between the second and third tank is 6 inches, giving ample space for free insertion of alundum thimble and at the same time not permitting the solvent while dripping from petcocks to cool to any marked degree. In practice, the second tank is heated to about 65° C. and the temperature of the syphoning of the soxlets 50° C.

With this apparatus, using the alundum thimbles, we have been enabled to get duplicates within 0.2 of 1 per cent. When a cotton mat is used, the extraction is very apt to be continuous in place of syphoning in which case the results are erratic.

The time of extraction is another important factor. Our most concordant results have been obtained by following the official method in extracting 30 grams of leather with 2,000 cc. of water in three hours. Longer time does not permit temperature control and a shorter period does not allow the temperature within the soxlets to reach the required heat without danger of overheating in some instances.

We recommend that a uniform method of sampling be adopted for each class of leather. And that the sample be prepared in some mechanical way so that the fibers will be long and silky. This we consider very important, for where too fine a preparation is attempted, the danger of burning the sample is very great. and unless a careful preparation is made, the sample is liable to contain lumps which are not in condition to be readily extracted.

As to the use of the alundum thimble in general, we would say that it is very convenient, easily cleaned and tends to give concordant and uniform results. This, we assert, when thimbles are used in connection with some suitable apparatus such as the one outlined above, or at least with cone shaped soxlets. We have used this kind of apparatus and have found that the results are comparable and valuable.

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NOTES ON THE ALUNDUM THIMBLE.*

By F. H. Small.

At the 1913 meeting of our Association the writer presented a brief paper (JOURNAL, January, 1915, page 32) describing a form of alundum thimble, and suggesting that it possessed certain advantages as a container for the material to be extracted when tanning materials are extracted in a Teas extractor. Thimbles prepared as described were tested the following year by a Committee of which J. M. Seltzer was Chairman, and his conclusion was that "extraction without the use of the thimble is more thorough than when the thimble was used." In addition he together with several other of the collaborators found no advantage or convenience in the use of the thimble. (JOURNAL, November, 1914, page 467.)

In the face of so unfavorable report it is perhaps rather presumptuous of the writer to ask you to listen to further remarks on the same subject, but on the chance that some beside himself may be so benighted as to still have a kindly feeling for the alundum thimble he would beg leave to present the results of some further study.

The conclusion of the Chairman referred to above concerning the incompleteness of the extraction when the alundum thimble was used was justified by the data, and this incompleteness, as was apparent from the comments of several members of the committee was due to the considerable amount of condensation water which passed down the walls of the extractor and did not percolate through the material in the thimble: The obvious remedy was so to alter the apparatus that all the condensation water must pass through the material in the thimble, and to do this by some sufficiently simple device so that the thimble would not become a nuisance rather than a convenience. The arrangement finally decided upon by Mr. Williamson of The Norton Co. and the writer was to constrict the top of the thimble and insert a double-wedge-shaped rubber packing between the thimble and the walls of the extractor. This device has been in use in the laboratory of The Graton & Knight Mfg. Co. for over a month and has been found both efficient and convenient. Extractions

* Read at the Atlantic City Meeting, May 28, 1915.

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made with porcelain plate and cotton side by side with the thimble and packing have given results as follows:

	Hemlock		Oak bark		Hemlock	
	Plate	Thimble	Plate	Thimble	Plate	Thimble
Total extract	26.4	25.4	22.2	22.1	23.6	23.2
Soluble extract	21.6	20.8	19.5	19.3	19.2	18.9
Soluble non-tannin	8.4	7.8	7.7	7.5	7.2	6.9
Tannin	13.2	13.0	11.8	11.8	12.0	12.0
Insoluble	4.8	4.6	2.7	2.8	4.4	4.3

	Quebracho		Oak wood		Mangrove	
	Plate	Thimble	Plate	Thimble	Plate	Thimble
Total extract	37.8	38.5	9.8	10.4	57.0	55.2
Soluble extract	34.0	34.8	8.5	9.0	51.4	49.8
Soluble non-tannin	3.6	3.4	3.9	4.4	14.0	13.5
Tannin	30.4	31.4	4.6	4.6	37.4	36.3
Insoluble	3.8	3.7	1.3	1.4	5.6	5.4

It is believed that the alundum thimble with rubber packing as described will insure as complete extraction as is possible by the present official method, thus meeting the essential criticism of the Seltzer Committee. As to its convenience, while the writer can no longer rashly assert that "*anyone* will immediately grant that it is both a time saver and a convenience" he has seen no reason to alter his personal views as expressed regarding both the convenience and the merit of the alundum thimble.

RECOVERY OF THE SLUDGE FROM THE SULPHIDE PROCESS OF DEPILATING SKINS.*

By John Helfrich.

The principle of the sulphide process for unhairing hides and skins in a tannery is to place the stock in paddles containing a solution of sodium sulphide and allowing them to remain there until the operation is completed. Sodium sulphide hydrolyzes when in solution as follows:

$$Na_2S + H_2O = NaOH + NaSH.$$

As seen by the equation, there is at all times a certain amount of caustic soda in the solution. This is the active agent in dissolving

* Read at the Twelfth Annual Meeting, A. L. C. A., May 28, 1915.

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the hair. What chemical change takes place, I don't know as I never had the time to delve into this particular line of chemical research. Considerable ammonia is generated as the distinctive odor is very noticeable in the atmosphere, around the sulphide paddles.

Taking into consideration the high nitrogen content of hair, I thought that if the sludge could be recovered it would be of value as a fertilizer material. A sample of the dried recovered sludge, showed by analysis to contain 8.53 per cent. nitrogen of which 3.92 per cent. was strictly available. It was found after numerous experiments that the sludge couldn't be filtered in its original state, either by sand filter beds or mechanical filters. I found that the addition of alumina sulphate to the liquor completely precipitated the sludge, so that it could be easily filtered by means of a sand filter bed. Tests conducted in the laboratory showed that it was necessary to add enough alumina sulphate to unite with the free caustic soda, to yield the following equation:

$$6NaOH + Al_2(SO_4)_3, 18H_2O = 2Al(OH)_3 + 3Na_2SO_4 + 18H_2O.$$

The amount of alumina sulphate necessary to add was found to be so great as to make the cost prohibitive. Experiments were then conducted with the idea of using a mixture of sulphuric acid and alumina sulphate. These were more successful, as the following tables will show.

In order to find a market for the recovered sludge it was found necessary to have the moisture contents down to 15 per cent. A 24-hour air dried sample of the recovered sludge contained 76 per cent. moisture. Equipment required to recover the waste would consist of pumps, settling tanks, filter beds and driers.

The following tables show the cost of operation and the income derived from the sale of the waste for a period of one year.

Amount of sludge daily—7,650 gallons.
Amount of dried sludge, 15 per cent. moisture recovered daily—3,360 pounds.
Amount of dried sludge for one year—504 tons.
Income derived from the sale of the sludge—$5,040.00

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I. Alumina sulphate as a precipitant 1,400 pounds daily.

Cost of alumina sulphate	$5,670.00	
Cost of labor	600.00	
Cost of coal for evaporation	900.00	
Total cost (not including interest charges or other overhead expenses)	$7,170.00	
Deficit		$2,130.00

A second experiment was conducted and the following results were obtained:

II. 700 pounds alumina sulphate, 400 pounds sulphuric acid } daily

Cost of alumina sulphate	$2,735.00	
Cost of sulphuric acid	1,020.00	
Cost of coal	600.00	
Cost of labor	900.00	
	$5,355.00	
Deficit		$315.00

A third experiment was conducted and the following results were obtained:

III. 784 pounds sulphuric acid, 128 pounds alumina sulphate } daily

Cost of acid	$1,998.30	
Cost of alumina sulphate	516.90	
Cost of coal	600.00	
Cost of help	900.00	
	$4,015.20	
Profit		$1,024.80

In conclusion I will say that these tests were conducted only in experimental way and on a small scale, but from the results obtained from the last test I am convinced that the plan for the recovery of the sulphide waste is of value to the tanner.

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SEWAGE DISPOSAL.*

By J. M. Seltzer.

The following facts on the disposal of tannery waste are based on information gathered at the tannery of Kistler, Lesh & Company, Lock Haven, Pa.

The tannage is vegetable and about 260 heavy hides are worked per day.

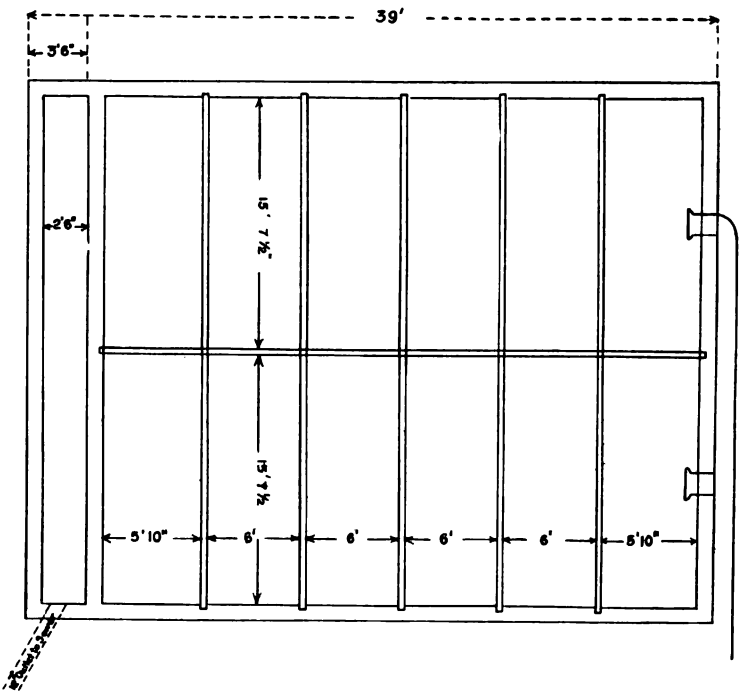

FIG. 1.—SEWAGE SETTLING TANK.

The total effluent per day is about 95,000 gallons, which is divided up as follows: Soaks 19,760 gallons, lime pits 7,560 gallons, bleach 6,480 gallons, yard 11,588 gallons and wash water about 49,500 gallons. The total effluent would be the equivalent of about 370 gallons per hide.

* Read at the Twelfth Annual Meeting A. L. C. A., May 28, 1915.

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The entire amount of sewage is passed through a sewage

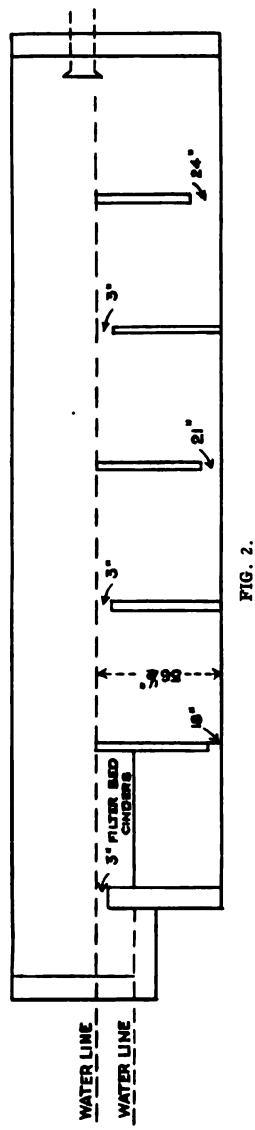

FIG. 2.

settling tank consisting of a double series of six settling vats which are shown in the diagrams. The cost of construction of

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this tank was $900.00. The annual cost of operating the system including interest, depreciation and labor is $227.00.

The composition of the effluent which passes from the above system is as follows:

	Pts. per million	Per cent.
Total solids	11,508	1.15
Volatile solids	6,454	0.64
Non-volatile solids	5,054	0.50
Nitrogen	111	0.01
Lime	1,280	0.12

The by-product from the above settling system is a brown sludge for which we have not as yet found a means of disposal. The composition of the sludge is as follows:

		Per cent.
Moisture on sample		82.64
Analysis of dry material		
Ash	61.27	
Volatile matter	38.73	100.00
Lime		35.27
Nitrogen		1.75
Phosphoric acid, P_2O_5		0.27
Fats		2.29

THE ANALYSIS OF TANNING MATERIALS.*

By Alexander T. Hough.

It is a recognized fact that the official method of analysis of the International Association of Leather Trades Chemists, even in its present improved form, leaves much to be desired from the point of view of accuracy.

Mr. Bennett's recent suggestions (J. S. C. I., 1914, 33, 1182, *seq.*), if finally adopted, will greatly enhance the value of the method, and it is to be regretted that the research work was not pushed to this point before the last change of method was made in 1907, as it was even then realized in which direction the present official method could be improved and made to give higher non-tannins.

The change which was then made reacted upon the trade incon-

* *J. S. C. I.*, May 15, 1915, pp. 472-3.

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veniently for some considerable time, owing to the apparent loss of tannin indicated by the new method; and at that time, if this loss had been still greater to the extent of the suggestions now made by Mr. Bennett, the resistance of the trade would probably not have been stronger.

The friction caused by the previous change of method passed, in England, in about a year. But on the Continent of Europe it was so great that the trade actually proved stronger than the chemists, and to this day, although the "shake" method is the official method of the I. A. L. T. C., it is only used on the Continent rarely, and by special request of the client; ordinarily the old filter bell method obtains, using dry chromed hide powder.

It will certainly be difficult to impose a second and still more sweeping change than the last on the English trade, and it seems rather futile to force more changes upon our own people when the continental and American trades will not fall into line as they ought to do, for the improvements suggested are equally applicable to all present methods of tannin analysis, and if adopted in England only will put English traders to a serious disadvantage.

In Mr. Bennett's first paper there is, however, one statement which appears to be misleading: he says that by increasing the dilution of the extract solution the non-tannins are increased, and he quotes figures showing that by adding 100 cc. of water to each 100 cc. of tannin solution shaken with 26.5 grams of wet chromed hide powder, an increase of non-tannins is obtained.

Now although the experimental work is correct and higher non-tannins are actually obtained under these conditions, the higher non-tannins are not due to dilution of the solution, but to the fact that 26.5 grams of hide powder is now being used to detannize 200 cc., whereas before, the same quantity was used to detannize 100 cc. The concentration of the hide powder has been decreased, and it cannot, therefore, do as much work in a specified time. If the quantity of tannin per liter of solution is decreased by 50 per cent., and 100 cc. be shaken with 26.5 grams of wet chromed hide powder, the non-tannin will actually be lower than with a stronger solution, for obviously, there being less tannin in the solution, it is more quickly absorbed, and the

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hide powder subsequently commences to absorb the non-tannins. That this is a fact may be proved by experiment. The difference is not great, but that only proves the efficacy of chroming the hide powder, one object of which is to reduce the absorption of non-tanning matters. Thus, by dilution of the tannin solution, lower non-tannins are obtained unless larger quantities of solution be used, or smaller quantities of hide powder, and the same result may be obtained by increasing the strength of the solution of tannin. Actually it would seem best to use tannin solutions of the present official strength and reduce the quantity of hide powder employed to such a point that detannization is just effected.

Then again Mr. Bennett suggests that the reduction of the quantity of hide powder employed may "involve some extension in the time of shaking." This seems as undesirable as it is unnecessary, for if changes are to be made, they should be as few as are necessary to obtain the desired degree of accuracy. Now the concentration of the tannin solution being constant, smaller quantities of hide powder take longer to detannize, and *vice versa*, since the present method uses a large excess of hide powder, there is no need to alter both factors—hide powder and time. The quantity of hide powder should, as suggested, be reduced to such a point that it will do its work in the official ¼ hour. If the detannization is not complete too little powder has been employed.

It thus appears that, so far as infusions of fresh tanning materials and solutions of tanning extracts are concerned, it is only desirable to change three factors, *viz.*: (1) The acidity of the hide powder before chroming, which should be reduced to *nil* by extending the method suggested by Dr. Parker and myself (*Collegium*, 1908, No. 310; this J., 1908, 229). (2) The reduction of the quantity of hide powder per "shake" to such a point that solutions of the present official strength are just detannized in ¼ hour. (3) The employment of a more basic chrome salt for chroming the hide powder.

In regard to tannery liquors I can only endorse Mr. Bennett's statements and eulogize his suggestions, excepting that which mentions dilution of the solutions for the estimation of non-tannins, to which the arguments instanced above apply with even

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greater force, owing to the larger quantities of non-tannins and free organic acids contained in such solutions. Back tannery liquors are usually somewhere between N/50 to N/20 in volatile acids, and the tannin strength is often within the limits prescribed by Mr. Bennett, so that these liquors would seldom require dilution before analysis, and acid solutions of such a strength and in presence of so little tannin would certainly seriously influence results. It is certain that the hide powder will primarily absorb the strong organic acids, thus automatically changing its condition and absorptive capacity before attacking the tannin.

I would suggest the possibility of reducing the acidity of all tannery liquors to some predetermined standard by first estimating the volatile acidity by the lime water method, or the concentration of the H-ions by means of the apparatus described by Wood, Sand and Law (this J., 1911, 872), then adding sufficient standard soda to neutralize to a certain fixed point—such as will leave the solution slightly acid, in order to prevent oxidation—and afterwards detannizing as suggested, but without further dilution. After detannization one might add to the non-tannins sufficient tartaric acid to combine with the added soda, together with an excess of 25 milligrams, and correct for sodium tartrate and tartaric acid in the final result. This is in order to expel all volatile acids as suggested by Mr. Bennett.

The washing of the hide powder has always been the *bête noire* of the "shake" method, and soon after the method was adopted in England it was suggested that this washing might be avoided by simply doing a blank test with distilled water and correcting the non-tannins by subtracting the residue thus found. A blank test with washed powder gives between 1 and 2 milligrams of residue, mostly organic, per 50 cc. evaporated. This residue precipitates tannin and is probably reduced to *nil* during shaking. The liquor squeezed from unwashed hide powder, however, gives a flocculent precipitate with tannin, and 50 cc. filtered and evaporated give a residue of about 223 milligrams, composed mostly of hydrolyzed hide substance or gelatones. In a blank test made with 26.5 grams of wet, chromed, and unwashed

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hide powder, shaken with 100 cc. of distilled water, 50 cc. of filtrate gave a residue of 32 milligrams.

On shaking this hide powder with tan solutions, one would have expected these precipitable gelatones to have been thrown out of solution at first, and absorption of tannin by the hide powder to have taken place secondarily. This, however, is not the case. By increasing the concentration of the tannin solutions shaken, the gelatones in the non-tannins decrease, as shown by the increasing feebleness of their reactions with tannin solutions and the decreasing differences between the residues yielded by washed and unwashed powders as the tannin strength advances (see table).

Eventually, by diminishing the hide powder employed, or increasing the strength of tannin, one might arrive at a point where no further cloudiness would be shown by the non-tannins on addition of tannin, but as this point would be always doubtful, and a correction therefore always variable, it would seem useless to attempt to do tannin analyses with unwashed hide powder.

Concentration of tan solution	Washed hide powder Grams	Unwashed hide powder Grams.	Difference Milligrams
0.37 Per cent.	0 0480	0.0600	12
0.185 Per cent.	0.0230	0.0390	16
0.074 Per cent.	0.0060	0.0280	22
Distilled water	0.0020	0.0320	30

In the experiments shown in the above table, 100 cc. of tan solution was shaken for ¼ hour with 26.5 grams of wet chromed hide powder—representing 6.5 grams of dry hide powder—and the residues given are on 50 cc. of the resulting non-tannin, evaporated and dried.

THE ANALYSIS OF TANNING MATERIALS: A REPLY.*

By H. G. Bennett.

(1) Some criticism is offered by Mr. Hough on the writer's suggestion to increase the dilution at which detannization is effected. The facts are, that when the same weight of hide powder is used to absorb the same weight of tannin, in the same man-

* *J. S. C. I.*, May 15, 1915, p. 473.

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ner, an increase in the dilution of the tannin infusion results in a smaller absorption of non-tanning matters. It seems legitimate to conclude that the change in the experimental results is the effect of the one deliberate change in the method of analysis. Other factors being constant, the dilution and the non-tannin percentage are concomitant variations, and are therefore causally connected. It is difficult to see how Mr. Hough can avoid that conclusion, but it is even more difficult to understand his positive statement to the contrary, *viz.*, "the higher non-tans are not due to the dilution of the solution."

Mr. Hough has apparently not realized that in experimenting on the effect of dilution, the ratio of the weight of hide powder used to the weight of tannin used was constant; and that in experimenting on the effect of a lower proportion of hide powder the dilution was kept constant. These are two different lines of experiment; the factors changed are fundamentally different, the results are affected to a different extent and for different reasons

(2) Mr. Hough also says that any extension in the time of shaking is "as undesirable as it is unnecessary." With this the writer is in full agreement. The method of procedure suggested has been used for over two years, and no extension of the time of shaking has ever been found necessary. Mr. Hough's quotation referred not to the revised method suggested, but to possible future experiments, the object of which was to ascertain the *smallest possible proportion* of hide powder which could be used for complete detannization. In employing 5 grams of hide powder per shake 15 minutes shaking is sufficient; but if it be desired to reduce the proportion of hide powder to the absolute minimum, *the attainment of this minimum* may involve an extension in the time of shaking. It may yet be found that the minimum amount of hide powder necessary for 15 minutes shaking does not give a sufficiently accurate result.

The writer is of the opinion that further experiments in this direction are very desirable, the attainment of this minimum being conducive both to truth and to concordance. The lower the proportion of hide powder, the less the method is dependent upon variations in its quality.

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RESULTS OF 1914 COMMITTEE ON EXTRACT ANALYSIS.

MYROBALAN EXTRACT.

No.		Per cent. total solids			Per cent. soluble solids			Per cent. insolubles			Per cent. non-tannins			Per cent. tannin			No.
		Slow	Rapid	Diff.	Slow	Rapid	Diff.	Slow	Rapid	Diff.	Slow	Rapid	Diff.	Slow	Rapid	Diff.	
1	Roy H. Wisdom . .	43.51	43.53	+0.02	41.86	42 21	+0.35	1.65	1.32	—0.33	15.90	15.81	—0.09	25.96	26.40	+0.44	1
2	F. M. Loveland . .	43.57	43.31	—0 26	41.57	41.52	—0.05	2.co	1.79	—0.21	16.10	15.63	—0.47	25.47	25.89	+0.42	2
3	F. H. Small	43.41	43.34	—0.07	41.55	41.86	+0.31	1.86	1.48	—0.38	15.66	15.91	+0.25	25.89	25 95	+0.06	3
4	C. M. Kernahan . .	43.45	43.32	—0.13	41.79	41.90	+0 11	1.66	1.42	—0.24	15.36	15.11	—0.25	26.43	26.79	+0.36	4
5	M. F. Nichols . . .	43.83	43.89	+0.06	41.53	41.92	+0.39	2.30	1.97	—0.33	15.93	15.86	—0.07	25 60	26.06	+0 46	5
6	C. R. Oberfell L. M. Richeson .	43.62	43.59	—0.03	41.81	42 00	+0.19	1.81	1.59	—0.22	15.63	15.88	+0.25	26.18	26.12	—0.06	6
7	F. O. Sprague E. A. Wallin . . .	43.56	43.50	—0.06	41.80	42.15	+0.35	1.76	1.35	—0.41	15.67	15.38	—0.29	26.13	26.77	+0.64	7
8	F. P. Veitch J. S. Rogers R. M. Frey . . .	43.13	43.85	+0.72	41.94	42.56	+0.62	1.19	1.29	+0.10	16.16	16.16	0.00	25.78	26.40	+0.62	8
9	W. K. Alsop	43.28	43.27	—0.01	41.08	41.05	—0.03	2.20	2.22	+0.02	15.46 15.42[1]	15.29 15.41[2]	—0.17 —0.01	25.62 25.66[1]	25.76 25.64[2]	+0.14 —0.02	9
10	J. M. Seltzer	43.55	43.44	—0.11	41.78	41.88	+0.10	1.77	1 56	—0.21	15.55 15.70[1]	15.59 15.66[2]	+0.04 —0.04	26.23 26.08[1]	26.29 26.22[2]	+0.06 +0.14	10
11	C. R. Delaney . . .	43.82	43 62	—0.20	41.97	41.94	—0.03	1.85	1.68	—0.17	16.32	16.10	—0.22	25.65	25.84	+0.19	11
13	W. A. Fox . . .	43.30	43.28	—0.02	41.24	41.26	+0.02	2.06	2.02	—0.04	16.03	15.93	—0.10	25.21	25.33	+0.12	13
	Average	43.50	43.50	0.00	41.66	41.85	+0.19	1.79	1.61	—0.18	15.78	15.69	—0.07	25.88	26.16	+0.28	

Slow = Slow cooling and slow chroming. Rapid = Rapid cooling and rapid chroming.

[1] Rapid chroming and slow cooling. [2] Slow chro ming and rapid cooling. [1] and [2] are omitted from averages.

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QUEBRACHO EXTRACT.

No.		Per cent. total solids			Per cent. soluble solids			Per cent. insolubles			Per cent. non-tannins			Per cent. tannin			No.
		Slow	Rapid	Diff.	Slow	Rapid	Diff.	Slow	Rapid	Diff.	Slow	Rapid	Diff.	Slow	Rapid	Diff.	
1	Roy H. Wisdom	47.33	47.41	+0.08	43.78	44.80 45.83[1]	+1.02	3.55	2.61	—0.94	8.36	8.32	—0.04	35.42	36.48	+1.06	1
2	F. M. Loveland	46.97	47.01	+0.04	43.69	44.06	+0.37	3.28	2.95	—0.33	8.50	8.61	+0.11	35.19	35.45	+0.26	2
3	F. H. Small	47.22	47.19	—0.03	43.68	43.96	+0.28	3.54	3.23	—0.31	8.14	8.17	+0.03	35.54	35.79	+0.25	3
4	C. M. Kernahan	47.15	47.30	+0.15	43.59	44.13	+0.54	3.56	3.17	—0.39	8.19	8.11	—0.08	35.40	36.02	+0.62	4
5	M. F. Nichols	47.74	47.67	—0.07	43.46	43.78	+0.32	4.28	3.89	—0.39	8.42	8.29	—0.13	35.04	35.49	+0.45	5
6	C. R. Oberfell L. M. Richeson	47.31	47.45	+0.14	43.42	44.13	+0.71	3.89	3.31	—0.58	8.09	8.19	+0.10	35.33	35.94	+0.61	6
7	F. O. Sprague E. A. Wallin	47.47	47.63	+0.16	44.37	44.61	+0.24	3.10	3.02	—0.08	8.16	8.25	+0.09	36.21	36.36	+0.15	7
8	F. P. Veitch J. S. Rogers R. M. Frey	47.62	47.95	+0.33	45.29	46.88	+1.59	2.33	1.07	—1.26	8.40	8.45	+0.05	36.89	38.43	+1.54	8
9	W. K. Alsop	47.28	47.13	—0.15	43.19	43.40	+0.21	4.09	3.73	—0.36	7.85 8.05[2]	7.96 7.93[2]	+0.11 —0.12	35.34 35.14[2]	35.44 35.47[3]	+0.10 +0.33	9
10	J. M. Seltzer	47.07	47.08	+0.01	43.80	44.23	+0.43	3.27	2.85	—0.42	8.06 8.13[2]	8.10 8.22[3]	+0.04 +0.09	35.74 35.67[2]	36.13 36.01[3]	+0.39 +0.34	10
11	C. R. Delaney	47.79	47.46	—0.33	44.62	44.75	+0.13	3.17	2.71	—0.46	8.59	8.70	+0.11	36.03	36.05	+0.02	11
12	C. C. Smoot, III.	47.94	47.89	—0.05	44.96	45.67	+0.71	2.98	2.21	—0.77	8.11	8.49	+0.38	36.85	37.19	+0.34	12
13	W. A. Fox	47.81	47.84	+0.03	44.09	44.44	+0.35	3.72	3.40	—0.32	8.48	8.41	—0.07	35.61	36.03	+0.42	13
	Average	47.44	47.46	+0.02	44.00	44.53	+0.53	3.44	2.93	—0.51	8.26	8.31	+0.05	35.74	36.22	+0.52	

Slow = Slow cooling and slow chroming. Rapid = Rapid cooling and rapid chroming.

[1] Clear to transmitted light. [2] Rapid chroming and slow cooling. [3] Slow chroming and rapid cooling. [2] and [3] are omitted from averages.

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REPORT OF 1914 COMMITTEE ON EXTRACT ANALYSIS.

The Chairman of this Committee, Charles R. Delaney, has been unable on account of ill health to prepare a full report, but he sent the results of the work of his Committee to the editor before the Atlantic City meeting. Several copies were made, and these were passed around at the meeting while the report of the 1915 Committee was under discussion. These tables of results on pages 374 and 375 are published so as to be available for reference and comparison.

REPORT OF 1915 COMMITTEE ON EXTRACT ANALYSIS. ADDITIONAL RESULTS.

By F. O. Sprague, Chairman.

I offer two additional sets of results for the 1915 Committee on Official Method of Tannin Analysis, one from Prof. Procter and H. Brumwell, and the other from John F. Church. My reason for sending these in is that Prof. Procter and Mr. Brumwell kindly consented to collaborate and as I knew the foreign mail would be delayed I wrote them that I thought we would be glad to publish them whenever received. So I hope that you can find room in the JOURNAL for them at an early date.

COMMENT.

H. R. PROCTER AND H. BRUMWELL: *Quebracho extract.* There is little difference in the speed of filtration and appearance of solution with rapid and slow cooling. A *slight* opalescence was observed in both cases. The non-tans were perfectly clear.

Hemlock Extract.—Solubles and non-tans clear quite easily in both solutions.

Myrobalans Extract.—The solubles of the slowly cooled solution clears quite easily, the rapidly cooled solution clears with less ease and takes longer time. The non-tans were perfectly clear.

Chestnut Oak Bark Extract.—Solubles both by rapid and slow cooling clear with ease. The appearance of the non-tans shows *slightly* more opalescence in the slow cooling than the rapid, and it was impossible to clear these solutions completely.

For comparison we tried filtering by means of the candle filter.

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You will note that in the quebracho extract (rapid cooling) the candle filter shows no insoluble. This is an extract which under ordinary circumstances we should have used a filter paper instead of candle.

In estimating the non-tanins, the hide powder used was of acidity as specified by the I. A. L. T. C. regulations. This of course is not strictly correct according to your regulations, but the work had been done before the error had been noted, and as time is of importance we thought it better not to delay in repeating. The amount of moisture in the powder was perhaps a little less than used in your detannization, but was regular throughout and is therefore comparative.

JOHN F. CHURCH: I might say that the slow cooling gives lower results in tannin and I am convinced that it is the only method to use as it is nearer actual factory conditions where of course hot solutions of extracts are not cooled so rapidly and the insolubles are thrown out normally.

H. R. PROCTER AND H. BRUMWELL.

Quebracho Extract.

	Slow cooling		Rapid cooling	
	Filter paper per cent.	Candle filter per cent.	Filter paper per cent.	Candle filter per cent.
Tans	34.7	34.6	34.9	35.9
Non-tans	9.5	9.5	9.7	9.7
Insolubles	1.4	1.5	1.0	0.0
Water	54.4	54.4	54.4	54.4
	100.0	100.0	100.0	100.0
Myrobalans Extract.				
Tans	24.7	25.6	25.1	25.5
Non-tans	14.6	14.6	14.7	14.7
Insolubles	2.0	1.1	1.8	1.4
Water	58.7	58.7	58.4	58.4
	100.0	100.0	100.0	100.0
Hemlock Extract.				
Tans	24.6	24.4	23.7	24.3
Non-tans	13.9	13.9	14.1	14.1
Insolubles	4.8	5.0	5.5	4.9
Water	56.7	56.7	56.7	56.7
	100.0	100.0	100.0	100.0

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Chestnut Extract.

	Slow cooling		Rapid cooling	
	Filter paper per cent.	Candle filter per cent.	Filter paper per cent.	Candle filter per cent.
Tans	24.0	23.8	24.1	23.7
Non-tans	19.0	19.0	19.0	19.0
Insolubles	2.5	2.7	2.4	2.8
Water	54.5	54.5	54.5	54.5
	100.0	100.0	100.0	100.0

JOHN F. CHURCH.

Quebracho Extract.

	Slow cooling	Rapid cooling
Total solids	46.20	46.16
Soluble solids	44.84	45.65
Insolubles	1.36	0.51
Non-tannins	10.58	10.76
Tannins	34.26	34.89

Myrobalans Extract.

Total solids	41.46	41.52
Soluble solids	39.80	40.42
Insolubles	1.66	1.10
Non-tannins	15.81	15.99
Tannins	23.99	24.43

Hemlock Extract.

Total solids	42.98	43.08
Soluble solids	39.11	39.83
Insolubles	3.87	3.25
Non-tannins	15.81	15.72
Tannins	23.30	24.11

Chestnut Oak Bark.

Total solids	46.13	46.10
Soluble solids	43.06	44.68
Insolubles	3.07	1.42
Non-tannins	20.88	20.95
Tannins	22.18	23.73

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NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES.

An exposition will be held at the New Grand Central Palace, New York, N. Y., during the week of September 20, 1915. The space to be devoted to the exhibits amounts to 23,000 square feet. American chemical products, apparatus and processes will be shown. Working exhibits will be in operation during the continuance of the exposition. A convention hall will be devoted to meetings of various chemical societies. An admission fee of 50 cents will be charged. Complimentary tickets will be issued to exhibitors and to members of chemical societies. Intending exhibitors should apply at once to National Exposition of Chemical Industries, New Grand Central Palace, 46th St. and Lexington Ave., New York, N. Y.

ABSTRACTS.

The Dickson Centrifuge System of Sewage Treatment. E. H. TRIPP. *J. S. C. I.*, May 31, 1915, pp. 517-524. The title of this paper is somewhat puzzling, as the Dickson system seems to be quite separate from the centrifuge process, although both may be applied to the same sewage. Alexander Dixon of Dublin observed that solid matter floated on the surface of a sewage-bearing stream below the point where the effluent from a brewery entered, but not above that point. Experiments showed that treatment of sewage sludge with yeast produced a fermentation which resulted in the separation of a part of the water, producing a sludge having 20 per cent. solids, as against 10 per cent. in the untreated sludge. The yeast treatment does not affect the nitrogen content of the sludge. In the practical application of the method at Dublin, the treated sludge is dried by a hot air process, using about 1 ton of coal to produce 1 ton of dried sludge, containing about 3 per cent. each of nitrogen and phosphoric acid. The high temperature of drying kills weed seeds which are a very undesirable constituent of many sludges. The action of the yeast takes place to the best advantage at temperatures from 90° to 96° F. The city of Dublin, at a cost of $2,500,000, has installed a plant, and has entered into a 25-year contract for the treatment of the whole of its sludge by the Dickson process. The sludge is mixed with 0.5 per cent. yeast, in suspension in water, and also with 3 per cent. of fermented sludge, and then pumped into a heater. The temperature is maintained at about 94° for 24 hours, when the solids come to the surface and the separated liquid is drawn off. The sludge is now transferred to a dryer, through which flows a current of air at 450° F. It has been shown that killed yeast is just as effective for the process as live yeast. After intro-

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duction into the sludge the yeast cells rapidly disintegrate and soon disappear. The action does not take place if the sludge be previously sterilized. The action is believed to be due to anaerobic microörganisms which feed on the yeast, and that the levitation of the solids is caused by escaping gases. About one-fourth of the nitrogen of the dried sludge is in "available" form. The organic matter present, about 45 per cent., is believed to contribute much to the manurial value of the material. It meets with ready sale at about $12 a ton. The cost of drying is about $5.10 per ton.

The greatest drawbacks to the treatment of effluents by percolating filters are the high cost of the installation and the necessity of expert management. Both of these are obviated by the centrifuge system, which also yields an effluent superior to any other in freedom from suspended solids and in quantity of dissolved oxygen. The apparatus consists of a hollow cylinder with small perforations, containing a quantity of sand which is held in place against the wall by centrifugal force as the cylinder revolves at the rate of 400 revolutions per minute. The entering stream of liquid strikes a revolving disk about one-half the diameter of the cylinder, which throws it against the sand filter in a fine spray. In its passage through the sand, the liquid is not only thoroughly aerated and deprived of its suspended matter, but colloidal matter is apparently broken down, precipitated and removed. The reduction in the quantity of dissolved solids in the effluent from the centrifugal (called also "hydro-extractor") supports the conclusion that nitrogenous organic matter undergoes decomposition and oxidation in its passage through the machine. The effect on bacterial life is remarkable, some recent tests indicating the total elimination of *b. coli.*

A plant for both Dickson and centrifuge processes has been in operation at Winnipeg for some time past. The city analyst there recently tested the effect of centrifuging on untreated sewage. The sewage was passed through a centrifuge, the effluent given a ½-hour treatment on a small contact bed and then centrifuged again. After one centrifuging, the sewage showed 10 parts per million free oxygen; after two, 13 parts. The table shows other results in parts per million.

	Solids				Oxygen consumed from permanganate	
	Total	Volatile	In suspension	In solution	3-minute period	4-hour period
Raw sewage	2758	1129	603	2155	152	360
Once centrifuged .	2328	628	242	2086	92	222
Twice centrifuged	1486	306	18	1468	26	58

The water supply has 1,100 parts per million dissolved solids. Other tests were made on the effluent from which sludge had been precipitated. Centrifuging reduced the albuminoid ammonia from 14 parts per million to 3, the oxygen consumption from permanganate from 85 to 9, and total solids from 1,970 to 1,020. Bacterial content before treatment was 81 million per cubic centimeter, with many *b. coli;* after, 1.1 million with no

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coli. Tests on live fish showed that the effluent from the centrifuge is not injurious to fish life. It is without odor, hydrogen sulphide being oxidized to sulphuric acid in the process. The centrifuging process is adapted to the handling of many trade wastes.

In answer to a question, Mr. Tripp said that the centrifuging of sludge previously treated by the Dickson process gave a drier product than could be otherwise obtained, and that it was higher in nitrogen than that remaining from the centrifuging of raw sludge, since in the latter case the nitrogenous matter is largely broken down and destroyed. The contact bed to be used between the two treatments is especially valuable because it utilizes the oxygen saturation produced by the first centrifuge.

Determination of the Biochemical Oxygen Demand by the Saltpeter Method in Stockyards, Tannery and Corn-products Wastes. ARTHUR LEDERER. *J. Ind. and Eng. Chem.*, June, 1915, pp. 514-16. The author compares the dilution method with the saltpeter method. In the former, sewage is diluted with fresh water of known oxygen content and incubated for 10 days, methylene blue being added in definite quantity. The decolorization of the indicator gives the point of deoxygenation of the mixture. The saltpeter method is not described in detail. It involves addition of a solution of sodium nitrate to the sewage, 2 molecules of nitrate furnishing 15 atoms of oxygen. The amount of oxygen thus used by the sewage bacteria is the same as that taken up from water in the dilution method. By suitable modifications, the method may be applied to each of the kinds of wastes mentioned in the title.

Notes on New or Seldom Used Tanning Materials. R. LAUFFMANN. *Collegium*, 1915, pp. 197-209. A number of materials were tested to determine whether they contain catechol tannins ("Protokatechingerbstoffe") or pyrogallol tannins or both. If the formaldehyde reaction gives a complete precipitation, so that the filtrate gives no blue coloration with iron alum and sodium acetate, the material is held to contain only catechol tans. If there is no precipitate, the material is assumed to contain only pyrogallol tans, while incomplete precipitation indicates a mixture. If the addition of lead acetate to an acetic acid solution produces no precipitate, a pure catechol tan is indicated, while the appearance of a precipitate may show either a pyrogallol tan or a mixture. If bromine water gives no precipitate, pyrogallol tans only are present; but a precipitation from bromine may mean either a catechol tan or one of several pyrogallol tans which give a precipitate with bromine. To these tests were added the color produced on treated cloth strips, and the acidity of the tannin. In what follows, the formaldehyde reaction is designated by *f*, the lead acetate reaction by *l*, the bromine water reaction by *b*, the color produced on the strips by *c*, the acidity (milligrams KOH per gram tannin) by *a* and acetic ether solubility by *e*.

Cuero bark comes from South America. The sample examined gave 16.8 per cent. tan (filter method). *f*, complete ppt.; *l*, no ppt.; *b*, heavy ppt.; *c*, brownish red; *a*, 44; *e*, 62.

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Marokko Wood.—Shake method, 19.0-22.6 per cent. tan. Resembles quebracho. *f*, complete ppt.; *l*, no ppt.; *b*, heavy ppt.; *c*, red-brown; *a*, 26; *e*, 89.

Afzelia Wood.—Tannin, 15.2 per cent. (filter, 15.7); non-tans, 1.4 per cent. *f*, complete ppt.; *b*, ppt.; *l*, slight ppt.; *c*, yellowish brown; *e*, 47.

Cassia Bark (Turwar).—From *Cassia auriculata*, East Indies. *f*, complete ppt.; *l*, no ppt.; *b*, heavy ppt.; *c*, brownish red; *a*, 129; *e*, 150.

Barbatimao Pods.—Pods of *Stryphnodendron Barbatimao* from Brazil. Tannin (filter), 27 per cent. Completely pptd. by *f*; *l*, no ppt.; *b*, ppt. after some time; *c*, brownish red; *a*, 83; *e*, 14.

Lingue bark (Persea) comes from Chile. Average of several samples, (filter) tan, 22.1 per cent, non-tan, 9.9 per cent.; *f*, complete ppt.; *b*, heavy ppt.; *l*, no ppt.; *c*, reddish brown; *a*, 50; *e*, 16.

Pangin.—Aparently the fleshy part of a fruit of unknown origin. Tan (filter), 20.5 per cent., non-tan, 13.9 per cent.; *f*, ppt.; *b*, ppt.; *c*, brownish yellow; *a*, 211, *e*, 21.

Guara.—Eitner's observations on this are quoted (Abstract, this J., Vol. 9, p. 241). It is the pod of *Paullinia sorbilis*, a kind of divi-divi, and occurs in commerce in the form of coarse meal. Tan (filter) 55.8 per cent., (shake) 51.0 per cent.; non-tans 18.0 and 22.8 per cent.; *f*, no ppt.; *l*, heavy ppt.; *b*, no ppt.; *c*, greenish yellow; *a*, 184; *e*, 39.

Karabin.—South American pod, formerly called "Vainille," apparently fruit of *Caesalpinia tinctoria.* Tan (filter), 30.3; *f.* and *b*, no ppt.; *l*, heavy ppt.; *c*, greenish yellow; *a*, 299; *e*, 57.

Sumac, from Turkey and the Caucasus. Turkish, tan (filter) 20.5 per cent., non-tans 13.9 per cent. Caucasian, tan (filter) 23.0 per cent., (shake) 20.0 per cent.; non-tans (filter) 17.5 per cent., (shake) 20.5 per cent. These sumacs were tested to see if they vary from pure Sicilian in their reactions. The Caucasian does not. The Turkish, however, gives a slight bromine ppt. and has a lower acidity (124 instead of 245), indicating that it is a mixture of catechol and pyrogallol tannin.

Mangue leaves, from Brazil. Tannin (shake) 31.6 per cent., (filter) 33.3 per cent.; non-tans (shake) 20.0 per cent., (filter) 18.3 per cent.; *l*, ppt.; *f*, partial ppt.; *c*, yellowish brown; *a*, 177; *e*, 21.

Bablah, pods of *Acacia Arabica*, from India. Tannin (filter) 20.2 per cent., non-tans 18.7 per cent.; *f*, partial ppt.; *b*, ppt.; *l*, ppt.; *a*, 281; *e*, 43.

Araca bark, from Brazil. Tan (filter) 18.4 per cent., non-tans 4.4 per cent.; *f*, nearly complete ppt.; *b*, heavy ppt.; *l*, slight ppt.; *c*, reddish brown; *a*, 69; *e*, 26.

Cascara bark, from San Francisco. Tan (shake) 25.0 per cent., (filter) 28.5 per cent., non-tans (shake) 13.0 per cent., (filter) 9.5 per cent.; *f*, *l* and *b*, like the last; *a*, 32; *e*, 29; *c*, brownish red.

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Cebil bark, from Argentina. Tan (filter) 17.0 per cent., non-tans 5.2 per cent.; *f*, partial ppt.; *b*, ppt.; *l*, slight ppt.; *c*, brownish red; *a*, 77; *e*, 56.

Elephant roots, the roots of *Elephantorrhiza Burchellii*, from German East Africa. Tan (filter) 17.5 per cent., non-tans 20.6 per cent.; *f*, nearly complete ppt.; *b*, heavy ppt.; *l*, slight ppt.; *c*, reddish brown; *a*, 78; *e*, 40.

Ganib roots, the roots of *Hydnora longicollis*, from German S. W. Africa. Tan (filter) 32 per cent.; *f*, ppt.; *l*, slight ppt.; *b*, ppt.; *c*, brownish red; *e*, 21.

Garouille is the root-bark of *Quercus coccifera*. *f*, partial ppt.; *l*, heavy ppt.; *b*, slight ppt.; *c*, yellowish brown; *a*, 167; *e*, 21.

Sunlethet Bones.—Under this name the Research Station received a material of unknown origin seeming to be the fruit of a Caesalpinia. Tan (shake), with seeds, 23.6 per cent., non-tans 16.0 per cent.; without seeds, tan 51.5 per cent., non-tans, 16.6 per cent.; *f*, partial ppt.; *b*, slight ppt.; *l*, heavy ppt.; *c*, dirty yellow; *a*, 297; *e*, 61.

The following are classed as catechol tans only: *Cucro, Cassia, Marokko, Afzelia, Barbatimao, Lingue;* as pyrogallol tans only, *Pangin, Guara, Karabin, Caucasian sumac, Mangue.* Mixtures, chiefly catechol, *Araca, Cascara, Cebil, Elephant roots, Ganib roots.* Mixtures, chiefly pyrogallol, *Garouille, Sunlethet bones.* Mixture, nearly equal parts, *Bablah.*

L. B.

The Absorbent Power of Plumped Hide Towards Several Vegetable Tanstuffs. EMANUEL KUDLACEK. *Collegium*, 1915, pp. 1-25, 59-80, 117-29. 163-79. The usual method of studying tanning by experiments upon hide powder or gelatine has the advantages of convenience and uniformity in material, but is misleading in many respects. The structure of the intact hide with its protective grain is so different from that of the disintegrated powder, that the physical changes of such importance in tannage may differ. The author's experiments were made with white hide in sweet liquors.

For material, limed calves heads were used, from which select, uniform pieces were cut, about 2 dm.^{2}, 3 mm. thick. After deliming with very dilute HCl, a salt solution containing some soda was used for de-acidifying at 30° C.; lastly, 5 washings of 5-6 hours with distilled water. The product contained 0.17 per cent. ash and 0.83 fat, consequently 99 per cent. dry hide. The remarkably low content of 17.24 N (Schröder's mean, 17.8) is attributed to the youth of the animal. To determine the water in each sample, a small strip was cut off, with pieces put back in water ½-1 hour, then drained 2-3 hours and both weighed, the smaller slip in a bottle; it was then dried in the air and finally in a vacuum. For the tannage concentrated stock liquors were prepared by battery extraction. After these (sterilized with chloroform and thymol) had settled for weeks, 6 liquors of 0.2, 5, 1, 1.5, 2 and 3 per cent. tans were prepared by dilution, again disinfected and after standing analyzed by the official

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method. The weighed pieces of hide were immersed in 1-2 liters of the respective liquors from 4 tan-stuffs, myrobalans, mangrove bark, fir bark (Fichte) and oak bark. The liquors were replaced after several days a week or longer, according to requirements, by fresh liquor, the used liquor being stored (after re-sterilizing) for analysis. This routine was repeated until the hides were tanned through. Then the collected residual liquors were analyzed. The hides were hung directly in the first two weak liquors, but the others were first diluted and brought up to standard concentration as soon as practicable.

The author next discusses the records of his experiments which are minutely detailed in 47 pages of tables and diagrams. The concentrations of the liquors were directly proportional to the specific gravities on the whole; for low concentrations, the gravities increase more rapidly. Since non-tans are lowest in specific gravity, and less colloidal, those tan-stuffs rich in non-tans, such as fir, give the highest total solids for equal densities. A further consequence of the varying proportions of non-tans is that for equal gravities mangrove is highest in tannin, then follow myrobalans, oak, fir.

The residual liquors from the separate tannages were analyzed and the results subtracted (after proper corrections) from the analyses of the original liquors. The figures for the "apparent" adsorption thus obtained were tabulated as tans and non-tans taken up by the hide by "difference." It was found in general that the adsorption was practically completed in the first 4-5 weeks. For example, the total tannage with 3 per cent. myrobalans was carried out in 151 days with 11 liquors, 17 liters in all. At first there is a rapid absorption of tannin, the non-tans making only 7.73 per cent. of total solubles withdrawn at the end of period 1. The rapid absorption of tannin continues through the first 5 periods while that of the non-tans increases until just exceeding the tans. A decomposition of tan-stuff and emigration of the products and non-tans out of the hide take place in the last stage. In the 6th and 7th period, there is a rapid decline; the absorption of total solubles becomes for awhile negative because the splitting off of non-tans exceeds the absorption of tans. The end results of the tannages with weaker liquors correspond in the main to those of the consecutive stages with the 3 per cent. liquors. Summing up, the absorption appears practically finished in the first 4-5 weeks. The speed depends upon the character of the tans and to be independent of the non-tans. Oak and myrobalan tans are absorbed the fastest, while mangrove and fir are considerably slower. At the beginning, the absorption of non-tans is very slight, but soon increases to greater proportion than present in the original liquor (compared with tans). The maximum of non-tan absorption is reached at the end of the period of the greatest tannin absorption. From then on there probably ensues a removal of the non-tans from the leather as well as of tan-stuff decomposition products manifest through a remarkable lowering of the corresponding numbers, finally becoming negative.

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On comparing the specific gravities of the residual liquors in the case of mangrove, equal gravities represent the same composition in fresh or used liquor. With myrobalans, because of the accumulation of non-tans, there is an increased amount of total solubles in the used liquor and this relation is still more marked with fir. Used oak liquors, on the other hand, contain a smaller amount of total solubles, tans and non-tans than fresh liquors of the same gravity.

Loss of hide substance during tannage was computed from the difference between dry pelt and hide as determined in the leather (Kjeldahl). This loss is the greatest in the leathers from the weak liquors and diminishes with increased strength. Von Schröder states the loss of hide in tannage to be slight. This is the case here especially with 3 per cent. liquors, which is nearest practice. In order to hinder loss of hide during tannage, it is necessary to supply tannin as fast as practicable with increased concentrations. The greatest loss occurs with myrobalans; this tan-stuff easily decomposes and the products are withdrawn from the hide, carrying away its substance with them. Next in order come fir, mangrove, oak. May not the poor rendement obtained with myrobalans be largely due to loss of hide? Even in the last tannage in 3 per cent. liquor there was a loss of 4 per cent. (on white weight) and 19.32 per cent. in the 0.2 per cent. liquor; in oak this last was only 8 per cent.

The leathers obtained from the various experiments were rinsed slightly and let dry for weeks at ordinary temperature. Contrary to expectation, the specific gravity of the oak leather was remarkably low although this material is rated as weight giving. Myrobalans leather was peculiar; its highest density was in those from the dilute liquors, then it sunk and reached in the 3 per cent. liquor the lowest value for any of the leathers obtained, although the amount of tan-stuff absorbed was very high. The gravity of the mangrove leather was proportional to the tannin absorbed and was the highest of all. The ratio was also directly proportional with fir. It is concluded that the specific gravity of uncurried leather is first of all dependent on the character of the tan-stuff and next, with some irregularities, on the amount absorbed. On subjecting the leathers to pressure by rolling, it was found that the specific gravity was raised the most (in percentage) for oak, then myrobalans, fir, mangrove.

The strengths of the various leather were also studied; although very low from default of currying, they may be compared. The mangrove leather was the lowest in every respect. Fir leather showed the highest breaking resistance and oak the greatest elasticity. Myrobalans gives hide very little leather character and the stretching power decreases with the tannage.

The solubles in the leather (loss by washing) always increased with concentration of the liquors used in tanning. Contrary to expectation, the highest loss was with oak; then myrobalans, fir, mangrove. The ratio of non-tans to tans in the solubles is much less than in the fresh liquors. The term "loss by leaching" (Auslauge verlust) is used here to designate

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the loss by further treating the already washed leather with boiling water. From this number is computed the water resistance according to Fahrion. In applying the hot water test, especial attention should be paid to the outward appearance of the leather. Here the myrobalans leather went completely into glue. The mangrove product was similar, though less marked; it was elastic on cooling. The fir and oak leathers shrunk somewhat, but formed no glue nor melted. Their resistance to heat is greater, and their loss by leaching small compared with mangrove and myrobalans leather.

The composition of the leather may be expressed either by percentage of constituents or by basing all constants on 100 parts hide which gives much the best viewpoint. All the leathers showed a regular decrease in hide substance with increase of strength in the liquor used, although the differences were not great, smallest for oak and mangrove, somewhat more for fir and myrobalans. A distinction is made between hide substance of leather substance and free hide substance in leather. Leather substance = fixed hide substance + fixed tannin. The free hide was determined while making the hot water test ("loss by leaching"). The extracts obtained were turbid, but clear while hot. The hot water dissolves unfixed gelatine which is afterwards precipitated by the tan-stuff which is also dissolved. Hofmeister has shown that the hydrolysis products from glutin give precipitates with tannin which are easier soluble in hot water than tanno-glutin itself. On filtering the leachings from myrobalans leather, the filtrate gave the gelatine reaction. By determining the N in the filtrate, the free hide substance could be computed. In this way 18.5 parts free hide were found in 100 parts total hide substance in the leather from the 0.2 per cent. myrobalans liquor. The smallest amount, 1.55 per cent., came from the leather of the 2 per cent. liquor. According to the content of free hide substance, myrobalans leather can be called the poorest tanned, and the oak leather the best since the amount was zero; mangrove and fir are intermediate. As to the tannage number (fixed tan), this increases with concentration of liquor, mangrove alone reaching maximum in the 1.5 per cent. liquor. Sometimes the number exceeded 100, reaching 138.3 with 3 per cent. fir; the others (same concentration) were myrobalans 118.4, mangrove 83.45, oak 104.3.

The rendement figures increase with the strength of the liquors. In all cases except with 3 per cent. myrobalans, the apparent absorption of tans by difference shows an excess compared with the rendement figures. This is a consequence of the decomposition of the tan-stuff, conversion into non-tan and also precipitation of tannin. W. J. K.

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CHANGES OF ADDRESS.

Charles R. Oberfell to 260 N. 3d. St. Philadelphia, Pa.

CORRECTION.

Page 358, July issue, line 8, for 35 read 354. Line 13 from bottom, for "lime was formed," read "lime was found."

PROPOSED PROVISIONAL METHODS.

MOELLONS.

Moisture.—Weigh accurately 3 grams of the sample in a wide platinum dish, and heat with a low flame until the moisture is all driven off. This point can be determined by the appearance

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of smoke and a slight crackling sound. Place the dish in a desiccator, cool and weigh.

Ash.—Ash the moellon remaining in the dish after the moisture determination in the usual manner, cool and weigh.

Unsaponifiable.—Weigh accurately in a 300 cc. flask, 5 grams of the moellon; add 2.5 grams caustic potash dissolved in a little water (or 5 cc. of a 50 per cent. KOH solution), and 25 cc. of 95 per cent. alcohol and boil with reflux condenser for 1 hour, shaking occasionally. Glass beads may be used to prevent bumping. Add 50 cc. hot water, cool, transfer to a separatory funnel and extract three times, using 40 cc. petroleum ether for each extraction. A little alcohol may be added to break persistent emulsions. Wash the combined ether solution three times with a mixture of 30 cc. of water and 10 cc. of alcohol, transfer to a tared dish, evaporate to dryness, cool and weigh. Excessive drying must be avoided.

Oxidized Fatty Acids.—Boil the soap solution remaining from the unsaponifiable determination until all the alcohol is expelled, then dissolve in hot water, transfer to a separatory funnel, rinse the beaker thoroughly into the funnel, bringing the volume to approximately 300 cc., and immediately add a slight excess of concentrated HCl (about 25 per cent. more than sufficient to neutralize total alkali). Rotate the contents of the flask vigorously, cool and shake out with petroleum ether. Run off the aqueous layer and pour off the ether layer, avoiding any loss of oxidized fatty acids. Wash these acids twice with small quantities of petroleum ether and hot water; dissolve in warm 95 per cent. alcohol, filter if necessary, transfer to a tared dish, and place in an ordinary evaporator and dryer for 16 hours; then cool and weigh. The entire operation should be conducted without delay.

Free Fatty Acids.—Weigh out 1 gram of moellon, dissolve in mixture of 20 cc. alcohol and 20 cc. sulphuric ether, which has been neutralized to phenolphthalein and titrate with N/10 NaOH, using phenolphthalein as indicator. Test for mineral acids or alkalies (by adding methyl orange to the water emulsion of the moellon) and if present make the necessary correction.

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HARD GREASES.

Titer Test.—Former provisional method, excluding description of standard thermometer.

Unsaponifiables.—Same as for moellons.

Free Fatty Acids.—Same as for moellons.

PROPOSED ADDITION TO OFFICIAL METHODS.

It is proposed to add to the first sentence of Section 10, Soluble Solids, the words "or Munktell's 1F," so as to read "S. & S. No. 590, or Munktell's 1F, 15 cm. single, pleated filter paper shall be used for the filtration."

PROPOSED CHANGE IN BY-LAWS.

A proposal for a change in the By-Laws has been received from A. C. Orthmann, as follows:

"That all Committee work under consideration and that which is to be presented at an annual meeting, be in the hands of the Editor of the JOURNAL sufficiently early for him to have it printed in the JOURNAL issued at least one month previous to the annual meeting, and that copies be presented to members present at the annual meeting."

COUNCIL MEETING.

A meeting of the Council was held Friday, July 2, 1915, at 2.00 P. M., at the Chemists' Club, New York City. There were present: Dr. L. E. Levi, E. J. Haley, H. C. Reed, W. H. Teas, T. A. Faust, F. H. Small. Dr. Levi presided.

The question of lactic acid was discussed, and it was decided that the whole question be referred to a committee, of which Lloyd Balderston is to be chairman, with the recommendation that if he is convinced of the accuracy of the method, that it is to be drawn up in shape to be presented to the Association for voting. This to be done as early as possible.

Alum Loading in Raw Stock.—After discussion it was decided that no action be taken on this at present.

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Moellons.—The recommendation of the committee was approved as a Provisional Method. (See page 177, JOURNAL A. L. C. A., April, 1915.)

Hard Greases.—The recommendation of the committee was approved, with the exception of the melting point, as a Provisional Method (JOURNAL A. L. C. A., May, 1915, page 241). The matter of the melting point is to be referred back to the committee to be John H. Yocum, F. P. Veitch; C. M. Morrison,

· *Free Sulphuric Acid in Leather.*—Decided that work on this be continued, with H. C. Reed as chairman of the committee.

Filter Papers.—The recommendation of the committee regarding the use of No. 1F Munktell's Swedish filter paper was approved for a vote. (See page 291, JOURNAL A. L. C. A., June, 1915.)

A committee on filtration was appointed, with F. H. Small as chairman, to work along lines suggested by him.

Tanning Materials in Admixture.—Moved and carried that the A. L. C. A. Advisory Committee take up this question with Pratt Institute and have them take up the work there, with the exception of the sulphite-cellulose admixture, which is to be taken up by a committee of which A. C. Orthmann will be chairman, and continue work with the use of reagent No. 33.

J. V. R. Evans was appointed chairman of the Committee on Methods dealing with analysis of materials in connection with beamhouse procedure. He is requested to try to draw up a set of methods for beamhouse materials, such as limes and sulphides, but not bates. C. R. Oberfell, C. C. Smoot, III, and John Helfrich are to be on this committee.

Moved and carried that no further work on the disposal of tannery waste be attempted at present.

Official Method of Tannin Analysis.—F. H. Small was made chairman of a committee to collect all available information and make recommendations as early as possible. He to select his own committee.

Alundum Thimble.—C. C. Smoot, III, was appointed chairman of a committee in regard to its use in extraction of tanning materials.

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Dr. Theodor Veit was made chairman of a committee to ascertain the feasibility of the use of the alundum thimble for filtration of soluble solids.

Sulphonated Oils.—Moved and carried that C. R. Oberfell be chairman of a committee to continue work, especially along the lines of ash and neutral fats. Also, that Rudolp Boehringer, Adolf Schubert, C. G. Burcke, and Charles Eachus be on this committee.

The matter of where the next annual meeting of the Association will be held was laid over till a later meeting of the Council.

Disinfection of Hides.—Moved and carried, that a committee be appointed with W. K. Alsop as chairman, others on the committee to be John H. Yocum, F. P. Veitch, C. M. Morrison, Fred A. Wallin, J. C. Smoot, and J. A. Connelly.

Proposal from A. C. Orthmann, regarding change in By-Laws, to take regular course and be voted on at the next annual meeting.

Uniform Blanks for Tannin Analysis.—A committee was appointed, with E. J. Haley as chairman, others on the committee to be T. A. Faust and H. C. Reed.

It was moved and carried unanimously that a vote of thanks be extended to *Hide and Leather* and to the *Shoe and Leather Reporter* for their kindness in furnishing advertisements of the annual meeting for two months previous to it.

The secretary reported the writing of letters of condolence as requested at the annual meeting.

NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES.

As mentioned in the July issue (p. 383) an Exposition of Chemical Industries will be held at the New Grand Central Palace, New York City, during the week of September 20, 1915. Through Mr. Charles F. Roth, manager, an invitation has been extended to every member of the American Leather Chemists Association to attend this exposition. The Secretary, Mr. H. C. Reed, 227 Fulton St., New York, will be supplied with passes for members of the A. L. C. A. Any member who wishes to attend the Exposition should apply to Mr. Reed for a pass.

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CHEMICAL CONTROL OF THE BEAMHOUSE.*

By John Hëlfrich.

In the manufacture of leather the first thing that the tanner takes into consideration is the quality of the leather to be produced from the raw stock that he is accustomed to tan and finish. It is a well known fact that the same beamhouse method used in working a Courland Scharren calfskin and then again on a Central Russian grasser will produce two different grades of leather. This is not due to the way they were worked through the beamhouse, but can be attributed to the initial difference in the character of the raw stock. The tanner is the best judge of the beamhouse method that gives him the most satisfactory results from the raw stock that he has to tan.

The next achievement to attain is uniformity; I mean by that the manufacture of a consistent product. All conditions being equal and the proper amount of supervision exercised, this can be accomplished. The proper beamhouse method having been decided upon, the step to insure uniformity is a chemical control of the various stages of the processes in the course of the manufacture of the skin into leather. It is absolutely essential that there is intelligent co-operation between the tanner and the chemist. It is necessary that the chemist be well informed concerning the various processes in the tannery if he is to be of any assistance to the tanner in maintaining uniformity in production or correcting any difficulty that may present itself. Don't think for one minute that I mean that the tanner should make any change in the processes of manufacture at the suggestion of the chemist, no matter how feasible it might sound, until the proposed change has been tried out in the experimental tannery and the effects of the change observed after the stock is finished. The idea that I wish to convey is that the chemist should maintain a complete chemical control over the various operations in the beamhouse.

To insure uniformity it is necessary that the conditions be the same from day to day. That is to say, if the weight of the stock going into the soaks is approximately 10,000 pounds daily and

* Read at the Twelfth Annual Meeting, A. L. C. A., Atlantic City, May 28, 1915.

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it has been decided, based on actual experience, that the soak pits can comfortably take 1,700 pounds dry or dry salted stock, let that amount be the standard and let the height of the water in the pits be constant. This applies to all containers such as lime pits, lime and bate paddles. Have a constant load and a constant level at all times.

I know from two years experience in the beamhouse that this system does produce a good uniform leather, and that a daily chemical check on the various operations gives a fund of information for future reference. In order to trace the stock through the various stages from the beamhouse to the finished product, it is necessary that each skin be stamped with a lot and pack number. This serves to identify the system of manufacture, providing suitable records have been kept.

Beamhouse Methods.—There are at present two different systems for the depilation of skins in the beamhouse; the lime process and the sodium sulphide process. Both have their distinct advantages and their disadvantages. The advantage of the lime and sulphide or the lime and arsenic method is that the grain is freed from all dirt and consequently more suitable for the manufacture of colors. In this process the hair is saved and is a source of revenue to the tanner as a by-product. The disadvantages are the danger of loose stock from over-liming; fine hairs and beamster scratches. The advantages of the straight sulphide process are that the troubles from fine hairs and beamster's scratches are eliminated and that this method produces a fine grain. The only disadvantage is the fact that the hair is lost and cannot be utilized as a by-product. The additional cost of materials in this process is counterbalanced by the decreased cost of labor over the lime process.

In this article I will not endeavor to explain the theory of the various beamhouse methods as they have been fully covered by other chemists. My only object is to show the results obtained from maintaining a chemical control in a tannery using both beamhouse methods.

Chemical Control.—The analytical methods for the system of chemical supervision of the various operations in the beamhouse will be described together with data obtained from actual practice.

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Soaks.—The important determination in this process is the amount of dissolved hide substance. It is customary to add to the fresh soak water a small amount of sodium sulphide to facilitate the soaking of dry skins. This is absorbed by the skins as repeated tests for the presence of sodium sulphide, using sodium nitro-prusside as a reagent, failed to show any trace of free sulphide. Therefore, it is not necessary to make any allowances for it in the titrations; a sample is collected after one hundred skins are hauled from the soak liquor.

The amount of dissolved hide substance in a soak liquor can be readily determined by Stiasny's method.

Place 200 cc. in a 250 cc. flask and add 20 cc. of a 5 per cent. solution of zinc sulphate. Make up to the mark and shake well and let stand for a few minutes and filter through a 15 centimeter folded filter. Titrate 50 cc. of the filtrate as a blank against N/10 NaOH, using phenolphthalein as an indicator. To another portion of 50 cc. add 10 cc. of 40 per cent. formaldehyde (previously de-acidified with barium carbonate) and titrate in like manner. Fifty cubic centimeters, titrated equals 40 cc. of the original sample. Difference between the two readings is due to the fact that amino acids (decomposition products of hide substance) condensed with formaldehyde are increased in acid character. "Wood" formaldehyde reacts with amino acids, forming methylen-amino acids, which are distinctly acid and allow a sharp titration with phenolphthalein as indicator.

1 cc. N/10 NaOH = 0.007868 grams of hide substance.

Calculations.

$$\frac{\text{Cc. N/10 NaOH} \times (0.007868 \times 25 \times 3.785 \times 100)}{(453.6)} =$$

pounds of hide substance per 100 gallons.

For the expression in brackets, you can substitute the factor 0.164.

Sodium Sulphide Process.—In the straight sulphide process, the hair is removed from the skins by running the stock in paddles containing a standard strength of sodium sulphide. This in solution hydrolyzes as follows: $Na_2S + H_2O = NaOH + NaSH$. The caustic soda is the active agent in dissolving the hair from the skin, the skin also absorbs a certain amount of the

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caustic soda causing it to swell. After a sufficient time has elapsed, the sulphide sludge containing the dissolved hair is run off and the stock washed in the paddles, with cold water, until such time as the judgment of the operator dictates that the caustic soda is well washed out of the skins. Then bicarbonate of soda is added to the paddle and the water shut off and the stock allowed to run for one hour. The bicarbonate of soda neutralizes the remaining caustic soda as is seen by the following equation: $NaOH + NaHCO_3 = Na_2CO_3 + H_2O$. It is absolutely necessary that no free caustic alkali remain in the skin if a strong grain is desired. After running an hour in the bicarbonate of soda solution, a sample of the liquor is taken and analyzed for the amount of $NaHCO_3$ still in solution, an excess showing that the operation is completed.

Method of Analysis.—Place 25 cc. in a beaker, add 25 cc. N/10 NaOH and 25 cc. of a 5 per cent. solution of barium chloride. Titrate excess of NaOH against N/10 H_2SO_4 using phenolphthalein as an indicator. The following chemical reactions take place:

$$NaOH + NaHCO_3 = Na_2CO_3 + H_2O$$
$$Na_2CO_3 + BaCl_2 = 2NaCl + BaCO_3.$$

Calculations:

25 — (Number of cubic centimeters of N/10 H_2SO_4 used to neutralize the excess of NaOH) = cubic centimeters N/10 $NaHCO_3$

1 cc. N/10 NaOH = 0.008405 gram $NaHCO_3$ ∴ cubic centimeters of N/10 $NaHCO_3$ ×

$$\left(\frac{0.008405 \times 40 \times 1{,}000 \times 3.785}{453.6}\right) = \text{pounds of bicarbonate of soda per 1,000 gallons.}$$

For the above expression in brackets, the factor 2.805 can be used.

Chemical Control of the Sulphide and Lime Process.

Physical data required.

Wet trimmed weight of the pack.

Amount of lime and sulphide used.

Capacity of the pits or paddles before the skins enter.

Baumé reading of the lime liquor.

An explanation in regard to the method of liming would be

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in order An effort is made to keep the load uniform, that is, approximately 3,000-3,400 pounds on the wet trimmed weight. The height of the lime liquors is kept to a constant level so that at all times the paddles contain 1,530 gallons. The stock first goes into a mellow lime, called for convenience the entering lime. There they remain for two days after which they are hauled out and put back into a new lime made up of lime and sodium sulphide together with a portion of the mellow lime liquor. After remaining in the liquor for two days they are ready to be unhaired. This last liquor I call for convenience sake, the old lime.

Method of Analysis, Available Lime.—A uniform sample is collected and strained through cheese-cloth to remove what hair may be in the liquor. The sample is very well shaken and as quickly as possible a sample of 25 cc. is collected by means of a pipette and placed into a liter flask, then made up to the mark with distilled water and allowed to stand for one hour. This insures that the lime will all be in solution. Titrate 50 cc. of the diluted sample with N/10 H_2SO_4 using phenolphthalein as an indicator, then continue the titration using methyl red as an indicator. Owing to the fact that when lime and sulphide are slacked together a certain amount of free caustic soda is present in the lime liquor, and is indicated by phenolphthalein and must be allowed for, the amount of caustic soda formed when sodium sulphide is in solution is approximately 50 per cent. (or to be accurate 47 per cent.) on the anhydrous weight. That is, in the particular brand of fused sodium sulphide used in the tannery these observations were made. Therefore, the difference between the two readings is due to one half of the amount of sodium sulphide present. By subtracting from the first reading obtained with phenolphthalein as an end point, a like amount corresponding to the difference between the two readings, you make the allowance for the caustic soda in solution and this leaves the amount of causticity due to available lime; 1 cc. N/10 H_2SO_4 = 0.0028 gram CaO.

Caustic Alkali and Total Alkali—Cc.—Filter the lime liquor through a folded filter. Pipette 25 cc. into a beaker, add 100 cc. of distilled water using phenolphthalein as an indicator against N/10 H_2SO_4.

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Sodium Sulphide.—A. To 25 cc. of the filtered liquor add 25 cc. of a 5 per cent. solution of cadmium chloride and then 15 cc. of acetic acid. Heat and filter, wash the precipitate with water slightly acidified with acetic acid. Dissolve the precipitate in dilute hydrochloric acid and titrate against N/10 iodine using starch as an indicator.

B. Titrate 25 cc. of the filtered lime liquor against N/10 zinc sulphate using lead acetate or sodium nitro-prusside as an outside indicator. 1 cc. N/10 I or N/10 Zn SO_4 = 0.00391 gram Na_2S.

I am aware of the fact that after slacking lime and sodium sulphide together a chemical change takes place forming a calcium sulphydrate Ca (OH) (SH). Be that as it may, yet it is to the advantage of the chemist that in his reports to the tanner he calculates the sulphides as sodium sulphide for that is what the tanner used at first. What interests the tanner is how much available lime is left, how much sodium sulphide is left and how much hide substance was dissolved in the lime.

Hide Substance (Bennett).—A. The difference in cubic centimeters in titration between the total alkali and the caustic alkali minus one-half the reading in cubic centimeters of the titration for sulphides is due to the dissolved hide substance in the lime liquor. This may not be as accurate as a Kjehldahl nitrogen determination, but it answers very well for a rapid daily check in controlling the limes.

B. *Stiasny's Method for Lime Liquors.*—Place 50 cc. of the filtered liquor in a medium sized beaker and add 100 cc. distilled water. Place 50 cc. of the filtered liquor in a beaker and redden with phenolphthalein. By means of a burette neutralize with 10 per cent. solution of acetic acid and then N/10 iodine is added to a slight excess. The liquor is then titrated with N/10 NaOH until again reddened by phenolphthalein end point and then 10 cc. of neutral 40 per cent. formaldehyde is added and the titration continued with N/10 NaOH until the end point with phenolphthalein is again reached. The number of cubic centimeters used in the last titration is due to the amino acids neutralized.

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Bate Liquors.

Caustic Alkali due to lime.

Titrate 50 cc. of the sample against N.10 H_2SO_4 using phenolphthalein as an indicator.

1 cc. N/10 H_2SO_4 = 0.0028 gram CaO.

Object is to test the alkalinity of the bate liquor due to calcium hydroxide.

Pickle Liquors.

Excess of acid.

Titrate 50 cc. of the liquor against N/10 NaOH using phenolphthalein as an indicator.

1 cc. N/10 NaOH = 0.0049 gram H_2SO_4.

Calculations:

$$(\text{Cubic centimeters N/10 NaOH}) \times \left(\frac{0.0049 \times 20 \times 3.785 \times 100}{453.6}\right) = \text{pounds } H_2SO_4 \text{ per 100 gallons.}$$

Factor for the expression in the bracket = 0.0818.

The object of maintaining a chemical check on the pickle liquors is that you can govern the acidity or basicity of the chrome tan liquors.

This system of chemical control has been in effect in a large tannery for a period extending over two years. During this time 1,000,000 calfskins and 275,000 coltskins were manufactured into leather. As the quality of the leather has been maintained it speaks well for the beamhouse system of the tanner and the uniformity with which he runs his plant. I am exceedingly grateful to the tannery Superintendent, Mr. W. W. Lambert, for his active co-operation with me that made this system a success.

In conclusion I will say that I realize that the system is not as yet perfect. I anxiously await the criticisms of my fellow leather chemists and hope earnestly that this field of chemical research, so long neglected, will yield results that will be of mutual benefit to the leather chemist and to the tannery superintendent.

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CHEMICAL CONTROL LIME PROCESS, PHYSICAL DATA.

Lot and pack numbers	62-10	46-5	46-6	46-7	63-5	63-11	46-9
No. of skins	500	500	500	500	620	580	500
Wet weight	2,641	3,050	3,040	3,050	3,424	3,200	3,000
Enter lime	1/11/15	1/14/15	1/15/15	1/16/15	1/27/15	2/3/15	2/10/15
Temperature	70	70	70	70	70	70	70
Baumé	1.0	1.0	1.8	1.0	1.7	1.45	1.25
Capacity	1,530 gal.	1,530 gal.	1,530 gal.	1,530 gal.	1,530 gal.	1,530 gal.	1,530 gal.
Weight of lime	79	90		90			
Weight of sulphide	13	15		15			
Hauled lime	1/13/15	1/16/15	1/18/15	1/19/15	1/29/15	2/5/15	2/12/15
Temperature	60	62	62	66	63	63	64
Baumé	0.9	0.9	1.3	0 9	1.6	1.3	1.1
New lime	1/13/15	1/16/15	1/18/15	1/19/15	1/29/15	2/5/15	2/12/15
Temperature	70	70	70	70	70	70	70
Baumé	1.9	2.0	2.3	2.0	2.4	2.2	2.14
Capacity	1,530 gal.	1,530 gal.	1,530 gal.	1,530 gal.	1,530 gal.	1,530 gal.	1,530 gal.
Weight of lime	105	120	180	120	210	192	180
Weight of sulphide	26	30	45	30	51½	48	45
Old lime	1/15/15	1/19/15	1/20/15	1/21/15	2/1/15	2/8/15	2/15/15
Temperature	61	65	65	65	62	63	63
Baumé	1.8	1.7	2.1	1.7	1.9	2.1	2.0

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ANALYTICAL RECORD, LIME AND SULPHIDE PROCESS.

Lot and pack	62–10	46–5	46–6	46–7	63–5	63–11	46–9
Enter lime.							
Available lime	65.0	73.0	114.0	73.0	75.0	69.0	54.0
Sodium sulphide	13.0	14.5	30.0	14.7	28.0	29.36	31.0
Caustic alkali	11.4	12.06	14.9	11.64	12.6	13.42	13.5
Total alkali	14.2	14.42	21.2	13.74	17.7	19.64	18.66
Hide Substance	—	—	4.5	—	2.385	4.62	1.43
Hauled lime.							
Available lime	42.0	40.0	88.0	43.0	43.0	42.0	20.0
Sodium sulphide	7.35	7.3	14.0	10.0	21.7	22.0	20.0
Caustic alkali	11.6	11.34	11.2	12.1	12.54	13.18	12.4
Total alkali	14.0	13.84	15.74	14.1	17.78	18.34	17.24
Hide substance	3.65	3.6	6.36	2.9	5.3	5.77	4.505
Lime absorbed	0 87%	1.08%	1.18%	0.985%	0.935%	0.843%	1.103%
Sulphide lost	5.65 lbs.	7.2	16.0	4.7	6.3	7.36	11.0
Gain in hide substance	3.65	3.6	1.85	2.9	3.915	1.15	3.075

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ANALYTICAL RECORD, LIME AND SULPHIDE PROCESS.--(*Continued.*).

Lot and pack	62-10	46-5	46-6	46-7	63-5	63-11	46-9
New lime.							
Available lime	136.0	134.0	187.0	110.0	185.0	162.0	185.0
Caustic alkali	14.84	14.96	15.4	14.1	16.24	17.18	16.16
Total alkali	20.86	21.36	24.4	21.12	26.12	27.18	26.02
Sodium sulphide	32.6	37.26	53.0	34.0	56.5	61.0	54.0
Hide substance	3.65	3.6	2.65	2.6	3.445	2.63	3.505
Old lime.							
Available lime	114.0 lbs.	74.0	140.0	90.0	94.0	105.0	123.0
Sodium sulphide	30.0 "	31.0	48.0	30.0	48.0	46.0	41.0
Caustic alkali	14.9	15.1	16.0	15.52	16.88	16.7	16.84
Total alkali	21.2	21.62	23.8	22.1	25.46	25.24	24.8
Hide substance	4.5 lbs.	4.8	4.91	4.5	3.7	4.77	5.04
Gain in hide substance	4.5 "	4.8	2.26	4.5	0.225	2.14	1.535
Lime absorbed	0.835%	1.965%	1.52%	0.82%	2.63%	1.78%	2.06%
Sulphide lost	2.6	6.26	5.0	4.0	8½.0	15.0	13.3
Total lime absorbed	1.705%	3.045%	2.70%	1.805%	3.565%	2.93%	3.103%
Total sulphide lost	8.25	13.46	21.0	8.7	14.8	22.36	24.3
Total hide substance lost	4.5	4.8	4.11	4.5	4.177	3.29	4.605

The results in the preceding table under caustic and total alkalis are expressed in the number of cubic centimeters of decinormal sulphuric acid used in titrating the liquors.

The available lime, sodium sulphide and hide substance are recorded in the actual number of pounds contained in the liquor.

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CHEMICAL CONTROL SODIUM SULPHIDE PROCESS LOT A46—COURLAND SCHAAREN.

Soaks

Pack No.	No. of skins	Dry weight lbs.	Hide substance in lbs. per 100 gal.	Excess of acid in pickle per 100 gal. lbs.	Excess of Bi-Carbonate of soda
5	500	1,525	1.995	0.405	Lime
6	500	1,520	1.036	0.431	Lime
7	500	1,526	1.19	0.343	Lime
8	600	1,620	1.08	0.4136	40 lbs.
9	500	1,500	1.192	0.308	Lime

LOT A62—POLISH CALF.

Soaks

Pack No.	No. of skins	Dry weight lbs.	Hide substance in lbs. per 100 gal.	Excess of acid in pickle per 100 gal. lbs.	Excess of Bi-Carbonate of soda lbs.
4	1,500	4,170	1.365	0.361	43.0
5	1,500	4,155	1.369	0.471	40.5
6	1,500	4,155	1.365	0.220	45.0
7	1,000	2,780	0.9581	0.189	45.0
8	1,000	2,780	1.369	0.275	39.0
9	1,000	2,780	1.68	0.678	42.0
10	500	1,380	1.68	0.370	44.0
10	500	1,380	1.68	0.431	Lime
11	1,000	2,770	0.9258	0.370	44.0
12	991	2,775	0.93	0.483	44.5

LOT A63—BUENOS AIRES CALF.

Soaks

Pack. No.	No. of skins	Dry weight lbs.	Hide substance in lbs. per 100 gal.	Excess of acid in pickle per 100 gal. lbs.	Excess of Bi-Carbonate of soda lbs.
1	620	1,718	1.42	0.3344	43.0
2	620	1,724	1.44	0.3265	41.5
3	620	1,718	1.322	0.2728	44.0
4	600	1,656	1.348	0.2110	43.966
5	620	1,718	1.348	0.167	Lime
6	600	1,668	1.322	0.290	38.0
7	590	1,622	1.322	0.211	40.0
8	600	1,668	1.478	0.2464	34.0
9	580	1,624	1.51	0.2288	41.0
10	571	1,565	1.036	0.3344	36.3
11	580	1,600	1.322	0 368	Lime

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F57 S. A. Horse Hides.

Pack No.	No. of skins	Dry weight lbs.	Hide substance in lbs. per 100 gal.	Excess of acid in pickle per 100 gal. lbs.	Excess of Bi-Carbonate of soda lbs.
1	250	4,365	1.09	0.308	42.5
2	250	4.365	1.08	0.5192	43.0
3	250	4,358	0.995	0.2376	47.5
4	250	4,370	1.14	0.246	45.0
5	250	4.354	1.14	0.220	45.7
6	250	4,363	1.144	0.265	47.5
7	250	4,370	1.0628	0.2816	45.0
8	250	4,365	1.134	0.290	43.0
9	250	4,360	1.08	0.360	46.0
10	250	4.355	0.934	0.378	46.0
11	250	4,360	0.984	0.290	41.0
12	250	4,360	1.166	0.352	40.0
13	250	4.360	0.854	0.3256	42.0
14	250	4.358	0.906	0.2728	36 0
15	250	4,365	1.088	0 3168	39.0
16	250	4,360	1.06	0.286	38.0
Average			1.06	0.31	43.0

Caustic Alkali Due to Lime in Wash Waters and Bates.

Pack No.	Wash waters			Bate after running 1 hour
	1st 10 minutes	2nd 10 minutes	At the end of 30 minutes	
C97-3	6.4	4.5	3.0	2.67
C97-4	6.3	4.8	2.3	2.94
C97-5	5.74	2.9	1.64	2.1
C97-6	7.46	5.0	3.1	2.7
C97-8	5.78	3.8	2.4	2.52
C97-9	5.1	2.58	1.56	2.53
C97-10	5.54	3.1	1.82	2.9
C97-11	4.7	2.8	1.3	2.1
C97-12	7.16	4.51	3.2	3.06
C97-13	9.30	5.46	1.88	2.47
C97-14	6.14	2.68	1.28	2.43
C78-7	3.25	1.89	1.2	1.91
C78-8	7.12	5.24	1.4	2.52
C96-6	6.8	5.1	1.76	3.34
C96-7	6.3	3.65	0.58	2.45
X6-1	4.02	2.94	1.16	3.48
X6-2	4.36	2.2	0.80	3.14
C94-10	4.06	2.68	2.07	3.69
Average	5.86	3.66	1.80	2.70
Grams CaO	0.016428	0.010248	0.005040	0.007560

The results in the above tables are recorded in the number of cubic centimeters of decinormal sulphuric acid used in titrating 25 cc. of the liquors with phenolphthalein as indicator.

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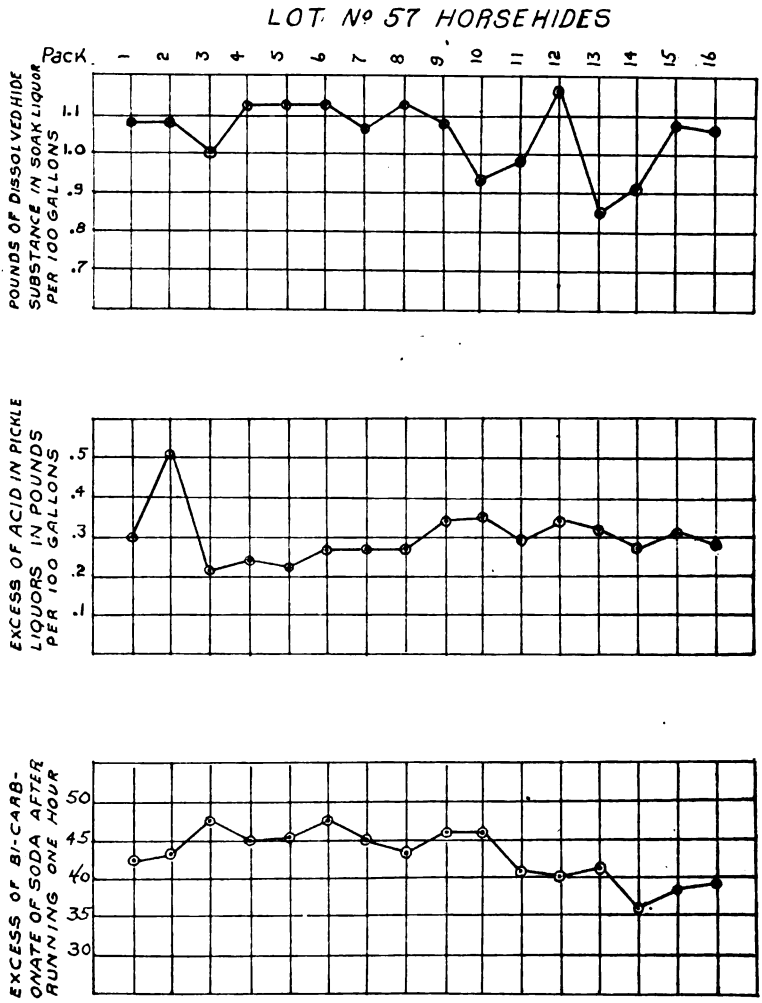

CHEMICAL LABORATORY,
ECLIPSE TANNING COMPANY.

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SULPHURIC ACID IN LEATHER.

Discussion at Atlantic City Meeting, May 28, 1915.

MR. J. S. ROGERS, chairman, being called on for a report, said: Several members of the Association signified their willingness to co-operate in the work of this Committee, but it was decided not to send out co-operative samples until some promising method had been developed.

The work has been very much handicapped by lack of time. Experiments have been carried out studying possible dialysis methods, and some work has been done on the Procter & Searle method. No satisfactory method, however, has been developed.

The results which have been obtained are not sufficient to justify, at the present time, conclusions or a detailed report. This work should be continued and a concentrated effort be made to develop a satisfactory method for the determination of free sulphuric acid in leather.

MR. REED: I have given considerable thought to the matter of a method of determining the amount of free sulphuric acid in leather recently, and it was brought to my attention particularly by analyses which we had to make in our laboratory of a red Morocco leather. We have used the Procter-Searle almost entirely in our work, and we reported this leather by this method. I think it had in the neighborhood of 0.8 per cent. free sulphhuric by the Procter-Searle method. We were asked then to make it by the absolute alcohol method. We did so, and found 0.11 per cent. free sulphuric. I endeavored to work out a method, and Mr. Norris did some experimental work along the lines suggested. I think I will briefly outline the method. I do not yet know whether it is of any value or not, but Mr. Norris did attain some results which seemed to indicate that it might have possibilities.

The trouble with the absolute alcohol method, as it exists at present, is not that it will not separate free sulphuric acid from sulphates, but that it will not separate free sulphuric acid from leather, the affinity of the acid for leather being very great. With this in view I thought it might be possible to in some way break down the affinity of the free sulphuric for leather and make the separation with absolute alcohol; so I took some book-binding leather and treated it first with acetone—or carbon bisulphide would answer the purpose just as well—in order to free it of any

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free sulphuric that was present. Then I digested the whole with strong nitric acid, which disintegrated it. I then evaporated off the nitric acid very carefully and took it up with absolute alcohol, and the separation seemed to be very good indeed. The absolute alcohol was filtered off, evaporated, the residue taken up with water and the sulphates precipitated with barium chloride in the usual manner.

With a leather which ran 0.8 per cent. free sulphuric with the Procter-Searle method I obtained 1.2 per cent. by this method. I believe the Proctor-Searle method too low This has been my feeling right along. I know that the absolute alcohol method, in its present form, gives entirely too low results. Work is under way now at the laboratory along the lines I have indicated to see whether the method suggested is a correct and workable one.

MR. VEITCH: It seems to me on first thoght that there is one point, in that method, that will need attention. That is being absolutely certain that all the nitric acid is removed. I do not know how completely it can be removed without other losses.

MR. REED: Of course we have looked into that feature of it. As you say the Proctor-Searle method undoubtedly gives a low result, except in the case where sulphonated oil is present, but ordinarily the tendency of the Proctor-Searle method is to give a low result. Absolute alcohol effects a good separation of sulphates and sulphuric acid when they are in a proper condition to make a separation.

MR. VEITCH: The difficulty is in getting the sulphuric out of the leather. That is the whole story.

DR. ROGERS: We have been doing quite a little work at the Institute and at the present time two of the chemical students are carrying on an investigation. They are trying a great many different ways of getting the leather into solution by means of peroxide and acid mixtures and crude alcohol method and a great many others, and it seems likely that at the end of the year they will have something here to help along the cause, as it seems very essential to get a good method. With this method two different workers can get concordant results. I think myself, however, that probably it is low. The leather in this particular case was not supposed to contain any sulphuric acid There was none used

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in the tanning but that does not mean that sulphuric acid could not have gotten into the leather, because they were pickled skins and acid was used in the coloring, and although the tanner does not use sulphuric acid it does not mean that it was not there.

MR. REED: I want to say further that this letter came from the American Institute of Mining Engineers. They wished to bind their periodicals and desired to have their leather tested prior to using it, and wrote me a letter, as Secretary of this Association, calling attention to the apparent differences obtained in the determining of the amount of free sulphuric acid, and asked that it be put before the Association and they further said that they would be glad, as an Institute, to co-operate with us in any way possible to help the cause along.

MR. VEITCH: It would be interesting to know in view of the fact that there is a difference in results on what is presumed to be the same leather—whether these samples came from the same or different skins. I have heard that from 0.8 to one-half per cent. were obtained by different analysts by the Procter-Searle method. It would be interesting to know whether the samples were all from the same skin—or from different skins where we reasonably might expect there would be a little difference in the acid content.

MR. REED: I do not believe we could tell that. They did not let us know whether it was from the same skin or not. I would like to know also by what method they found no free acid.

MR. ROGERS: The Procter-Searle gave a decided acid reaction, while by the dialysis method we obtained only a very slight reaction.

MR. BALDERSTON: In regard to the matter which Mr. Veitch first brought up, as to whether these samples were from the same skin, I do not think, unless the sample was ground and mixed before distribution that it would make any difference. I imagine that two samples taken from different parts of the same hide would not show anything like the same percentage of acid.

MR. ROGERS: I agree with Mr. Balderston. On some work we have been doing on the application of acid to leather we find that it collects around the outer edges of the leather more than in the center and it undoubtedly would make a great difference

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from what portion of the hide the sample was taken. It would also depend on how the acid was applied and how the leather was dried.

MR. LEVI: In the loose portions of the skin the acid will vary greatly, that is the flank, the shank and the belly, as compared with the back.

ANALYSIS OF SULPHONATED OILS.

Discussion at the Atlantic City Meeting.

MR. FAUST: There have been some manufacturers of sulphonated oil who want to know what has been done on the subject of neutral fats. Mr. Barton might tell us what he has in mind.

MR. GRIFFITH: Are there any members of the Committee present?

MR. BARTON: There seems to be a wide difference of opinion among the chemists as to the value of the different units. You talk to one chemist and he will use the moisture and unsaponifiables as the leading factors, another will lay stress on other points. Speaking from the standpoint of the manufacturer I would like to say that we have no protection whatever for giving a basis of settlement. Sometimes we are forced to guarantee a degree of sulphonation and on submitting samples to two different chemists you will find that they use two different methods for determination. I believe there should be some uniform method of analysis so that we would know just where we were when we sent our samples out, either to the tanners or to the chemist, and would suggest that a Committee be formed to adopt some standard form, the same as you have on Extracts. I would not have any suggestions to offer.

MR. ORTHMANN: Does not our official method for sulphonated oil cover what the gentleman wants?

MR. GRIFFITH: My understanding is that it does.

MR. BARTON: It would be true if every manufacturer was using the same method of sulphonating oils. I think you will find from the results that have been obtained on different oils, that have been sulphonated, that the official method is not worth

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a whole lot. To illustrate that: take an oil that has been neutralized with a fixed alkali—with soda ash, or potash and one neutralized with ammonia you will find that the official method there in taking the total fat shows a very wide difference. I have here a couple of analyses which show from 65 to 66 per cent. total fat, which corresponds very closely with the factory figures. Taking the official method you will get about 7 to 8 per cent. higher total fat. In this particular oil it is not true that it contains this higher percentage.

I might add to that that I have worked on the method Mr. Eachus advanced, and I found his methods result very closely to the figures we get from the factory. I do not know whether that would hold on different oils.

MR. EACHUS: About two years ago I proposed a method. It was to neutralize the free fatty acids and sulphonated fatty acids with a normal caustic soda solution, and then shake out the neutral oil with petroleum ether. That would be all right for sulphonated cod oil, or any sulphonated oil but castor, but I made a mistake in suggesting petroleum ether for all oils as it would not do for castor oil.

That method was tried out along with the Lewkowitsch method, but the chemists came to no satisfactory conclusion. I have not done any further work and I have not planned any work. I thought I would leave it to the younger chemists to work upon this method. I proposed the method, let them try it. I think it is a good method.

MR. ORTHMANN: I propose that we appoint a Committee to investigate a method of determining the total fat similar to the Lewkowitsch method. There is a method by Herbig (see p. 437) and it seems to me it is a very good method. It is digesting the sulphonated oil with hydrochloric acid in a reflux condenser, and washing with water and dissolving the oil in sulphuric ether.

It seems to me that the most important point there is the total fatty matter, and the next point the completeness of sulphonation. I have used this method for some time and get good results from it.

MR. GRIFFITH: Mr. Oberfell is the chairman of the old committee and could probably be reappointed. The difficulty has been

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to get members of this Association to serve on the committee. That has always been the difficulty with requests of this kind—to get members who will volunteer to do some work.

MR. ORTHMANN: I will be one of the first ones to volunteer.

MR. GRIFFITH: The report of these proceedings will come before the Council, and those who have been anxious to contribute to the work will be called upon to serve on that Committee. Unfortunately, Mr. Oberfell is not here. He was the chairman. I do not know whether that Committee has been dissolved by virtue of having sent in its report, but certainly another Committee will be formed in any case.

COLOR DUE TO COPPER EXTRACTORS.

By T. G. Greaves.

The coming of the time in extract manufacture when small differences of color are of material interest has been hastened by competition with European extracts in European markets where a large part of the American product is notorious for its bad color. In the consideration of the comparative effect on the liquor of extraction in copper and glass the color quality of the liquor produced is now, from an industrial point of view, of fully as much importance as a small difference of the tannin yield.

Mr. H. C. Reed has discussed the possibility of a difference in the tannin yield of raw materials as extracted in copper and glass, in his report as Chairman of the Committee on Extraction in 1907, and Messrs. C. R. Oberfell and L. M. Richeson have determined the question by their work published in the JOURNAL of January, 1914, but neither of these discussions have any suggestion as to the comparative colors of the extracts. They have treated the question from a purely analytical point of view, and perhaps refrained from mentioning the color because it seemed too valuable a suggestion to give away at that time. It seems to be generally held now by extract manufacturers, however, that copper has a definite, though not very great, harmful effect on the color of the extract and the following tests were carried out by the writer in the laboratory of Jno. H. Heald & Company, to

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measure the effect of the copper apparatus on the color of the product.

The analyses made in connection with the color determinations were of only secondary interest, but as they illustrate the method of leaching used they will be briefly discussed. As would be expected from the work of Messrs. Oberfell and Richeson, in the mild treatment of these extractions, it seems that there was probably no loss of tannin due to the boiling in the copper apparatus. The entire percolate was collected on the outside in 8 hours after 40-minute periods of standing on the wood in an open jacket of boiling water. In each case the extraction in copper gave a tannin figure for the wood approximately 0.2 per cent. (averaging 0.20 per cent.) higher than the extraction in glass, and the soluble solids of the copper extraction were also uniformly higher than those of the glass (averaging 0.36 per cent. higher) due to the better conduction of the copper carrying more heat to the wood from the boiling water jacket and extracting it more fully. The opposite of this should be the case commercially where the heat is from the inside. The quantities of wood and water used were such that the average extraction did not reach the maximum by one-half of 1 per cent. The purities were fairly uniform, the glass averaging 71.9 against 71.7 for the copper, as might be expected from the somewhat more complete extraction in the latter case, and from the copper being slightly dissolved by the tannic infusion.

Color Due to Copper Extractors.

The particular mode of extraction alluded to was adopted for the following reasons: being mild, the material of the extractors only is involved; the extraction is not carried to the maximum because it is not so extracted at the mill; the color and per cent. tannin and degree of extract are, in extractions such as these, directly proportional so that a small difference of the degree of extraction does not affect the color because it is corrected to a standard tannin strength.

The color of extracts has not received as much attention in this country as it would have received if there had been a satisfactory standard method of color measurement. The color tests which follow were made on the Schmidt and Haensch colorim-

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eter, as modified by G. A. Kerr.* The guarantee by the makers of the Pinatype aniline colors that they will remain unchanged after months of exposure to the light, which Mr. Kerr mentioned, does not seem to refer to the dilute solutions, for the "Pinatype Red F" fades almost entirely in from 2 to 3 months, away from direct light, and the other colors are somewhat changed though not so much. Professor Procter and also G. A. Kerr are on the lookout for permanent color solutions that can be used in any suitable style of colorimeter. For determinations made at near the same time, however, the colors suggested in Mr. Kerr's paper are a trutsworthy means of comparing color values in an itemized way when used by a person experienced in using color solutions, and with the exercise of the time and care necessary for any colorimeter detetrmination.

The following figures are cubic centimeters of color solutions corrected to a standard strength of 0.4 gram tannin to 100 cc., so any small difference of leaching due to apparatus is corrected.

Chestnut wood extracted in	Yellow	Red	Blue
Glass	3.8	6.3	1.50
Copper (old)	5.1	9.1	2.30
Due to copper	+1.3	+2.8	+0.08
Glass	3.7	6.0	1.40
Copper (old)	5.4	9.4	2.40
Due to copper	+1.7	+3.4	+1.10
Glass	3.6	5.8	1.40
Copper (new)	3.6	6.8	1.70
Due to copper	+0.0	+1.0	+0.30
Glass	2.5	6.8	1.25
Copper (new, acid washed)	2.7	8.1	1.52
Due to copper	+0.2	+1.3	+0.26
Glass (average)	3.4	6.2	1.39
Copper (average)	4.2	8.4	2.01
Due to copper	+0.8	+2.2	+0.62

Color Due to Copper Extractors.

The two extractions of each of the four sets were of the same wood and leached and analyzed for tannin and color as duplicates. The copper extractors had no solder inside. In the first

* Journal A. L. C. A., Nov., 1914.

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two sets an old extractor, which was thoroughly soaked and washed with hot water, was used; in the third set one made of new copper, never used before, and in the fourth set the same new one washed in dilute acid to free the surface from copper compounds was employed. As is seen from the table the copper does not have so much effect when clean and new, but in every case extraction in copper gave a worse color than extraction in glass.

THE EXTRACTION OF VALONIA.*

By L. Balderston.

Just at present valonia has perhaps a rather slender practical interest for the tanner. The following results of some experiments on this material may, however, still have some academic interest, and we all hope the time may soon come when this valuable crop will again appear in the markets of the world.

Last summer we had occasion in the Elk Tanning Company's laboratory to make some leaching experiments on valonia cups. Our first discovery was that the ground material must be wet before putting it into our small leaches; otherwise its swelling when wet plugs the leaches so tightly as to prevent the water from passing at all. At first the new material was wetted with liquor pressed over from the preceding leaches, but this involved so much extra labor that in the next series of runs the fresh material was simply soaked with water, and the leaching in this case was quite as complete as in the other.

Compared with other materials with which we have experimented, valonia is remarkable in suffering so little loss of tannin by long heating. The percentage of tannin obtained in the liquors obtained from a given lot by leaching 144 hours in a series of six leaches, a new head being introduced every 24 hours, was almost exactly the same as that found by analyzing the same lot by the official method. The average of three simultaneous analyses gave 34.0 per cent. tannin, the highest being 35.4 and the lowest 32.3. The spent material, extracted by the official

* Read at the Atlantic City Meeting, May 28, 1915.

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method, gave 1.0 per cent. more, a total of 35.0 per cent., or 30.4 per cent. on the basis of the air-dry cups.

A puzzle presented on attempting to reduce the analysis of the spent to the basis of the air-dry new basis, since the ordinary method could not be used. To bring out the difficulty fairly, let us look over the usual process. A spent material is presented, the analyst having no knowelge in regard to what percentage of the original substance has been extracted. Before he can reduce his results to the basis of the new material, he must have a new sample, analyze it, and then assume that the insoluble residue left at the end of the analysis bears the same proportion to the whole new material as that left at the end of the analysis of the spent. In other words, he assumes that of the original material a certain portion is water, another definite portion water soluble, and a third definite portion insoluble. Knowing then what proportion of the original material is represented by this dry insoluble, it is easy to calculate how much new material is equivalent to the spent used in the analysis, and so to convert the analysis to the new basis. Thus if a hemlock bark showed 12 per cent. moisture and 22 per cent. extractive material, the insoluble residue would be 66 per cent. of the whole. If we find in a dry spent sample of this bark 4 per cent. total extractive, we assume that the insoluble 96 per cent. of the dry spent is equivalent to the insoluble 66 per cent. of the air-dry new. Therefore, the air-dry new was 96/66 of the dry spent, or to put it in the most convenient shape, the dry spent is 66/96 of the air-dry new, or 11/16. Now if the dry spent has 1.5 per cent. tannin, this will be 11/16 of 1.5 per cent. on the air-dry new, or about 1.0 per cent. In the case in question the whole of the spent was equal to the supposed insoluble residue of the new, so it was necessary to make some kind of a compromise assumption in order to reduce our spent analysis to new basis.

One lot of spents were started in the extractors in the afternoon, and the usual directions left for the watchman to turn out the burners in the small hours. But the watchman that night was a substitute who did not know his business, so the extractors ran till 8 o'clock in the morning. Two of these samples were run again the regular time. Both sets were in duplicate, the

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regular one showing very good agreement, the other not so good. The two sets of results were as follows in percentages of dry spent:

	Sample I		Sample II	
	Regular	Overtime	Regular	Overtime
Total solids	11.55	14.13	9.26	11.34
Soluble solids	10.35	12.87	8.56	10.40
Non-tannins	4.73	6.52	4.65	5.86
Tannin	5.62	6.35	3.91	4.54

The longer extracting of the spents having given so much higher figures, an effort was made to determine how long a sample would continue to yield appreciable amounts of soluble material. A 60-gram sample from 6-day leaching was run 8 hours in a Teas extractor, showing in per cent. on dry basis total solids 5.89 and tannin 1.98. Another extraction of the same, continued 16 hours, gave total solids 2.98, tannin 0.81. A third extraction of the same sample, run 24 hours, gave total solids 3.52, tannin 0.55. This was continued for 12 days, total solids only being estimated after the second day. On the twelfth day, or the eighteenth, counting the original leaching, 0.37 gram of solids was extracted. The only possible conclusion from this is that to arrive at the ultimate insoluble residue in the case of valonia is a process requiring much patience, and that the reduction of spent analyses to new basis calls for ingenuity. The total amount extracted in the 12 days was 16.88 grams, or about 29 per cent. of the dry spent. After about the third day, the clear yellow extract contained no tannin.

In order to relate the amounts extracted to the original material, a fresh start was made. A charge of 75 grams of new valonia, moisture 10.3 per cent., was divided into two portions, which were extracted separately in an alundum thimble, 4 lots of liquor, 500 cc. each being taken from each portion by outside extraction. The portions were then united and run under a reflux condenser for 24 hours. The liquor was then made up to 5,500 cc. and analyzed, giving an average on close duplicates of 57.59 per cent. total solids and 34.3 per cent. tannin, dry basis. This is 4 per cent. more total solids and 0.3 per cent. more tannin than were obtained by the official method. The sample was now run another 24 hours, yielding 3.24 per cent. total solids and 1.01 per

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cent. tannin. A third day's extraction gave an extract showing only a slight trace of tannin by the gelatine-salt test and having 2.09 per cent. total solids. Further successive 24 hour runs gave 1.37, 1.04, 0.75, 0.64, 0.55, 0.38, 0.37, 0.33, all these estimated on the dry matter in the original sample The residue was now dried over night on the steam oven, and again extracted for 24 hours, yielding an additional 0.85 per cent. The thimble and its contents were now again dried and weighed, and again extracted for 24 hours, the total solids this time being 0.69 per cent. of the original dry matter. This process was carried two steps further, the yields being 0.55 per cent. and 0.32 per cent. Calculating the total percentage of the original dry material extracted in 15 days from the addition of successive results gives 70.7 per cent., while the estimation based on weighing the final dry residue is almost exactly 1 per cent. more. Nearly all the material dissolved out of the original sample is, therefore, accounted for in the extract, very little having been lost in consequence of the 24-hour periods of boiling.

Having read H. G. Bennett's paper on the tannins of oak-wood, valonia and chestnut, reprinted in the JOURNAL for March, it occurred to me that the yellow substance he obtains by treating the water solution of the material obtained by dry distillation of valonia extract with an excess of bromine water might be characteristic of the non-tannins rather than of the tannin of the valonia. Mr. Bennett's experiment was accordingly repeated with solid valonia extract, a copious yellow precipitate resulting. Several liters of the extract obtained in the above experiment after the tannin was all extracted were now evaporated, and the residue subjected in the same manner to dry distillation and treatment with bromine. A yellow color resulted, and it seemed that the reaction was the same, although less pronounced on account of the smaller quantity of material.

The yellow color of the tannin-free extract suggested quercitron. A bunch of white wool yarn was mordanted with tin chloride and boiled a few minutes in some of the extract. All the color was discharged from the liquor, and the wool was dyed a good straw yellow, quite fast to soap and water.

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NOTE ON THE ADDITION OF FAT TO TANNIN EXTRACTS.*

By Puran Singh.

(Chemical Adviser, Forest Research Institute, Dehra Dun.)

Some of the cheaper tannin extracts, such as mangrove, have two great defects, *viz.*, their deep red color and harsh tannage. The best way to overcome the color difficulty lies in the judicious mixture of pure, unadulterated extracts with light-colored tanning materials in the tanyard. But very little seems to have been done by the tannin extract manufacturers to overcome the defect of harsh tannage. The last portion of this paper embodies the results of experiments carried out to overcome this defect. The suggestion came from the work carried out in connection with the fat content in tan barks which forms the first part of this paper.

The Probable Rôle of Fat in Tan Barks.

It has been noticed that well-known tanning materials giving soft tannage contain naturally more fat than others giving harsh tannage, as is shown in the following table. The air-dried barks were finely powdered and extracted with hot petroleum spirit till they were free from fat. The following were the results obtained:

Name	Moisture Per cent.	Tannin Per cent.	Total petroleum spirit extract Per cent.
Materials giving harsh tannage—			
Sal bark (*Shorea robusta*)	10 60	6.55	0.14
Terminalia tomentosa bark	6.70	10.76	0.18
Mangrove extract	13.43	70.20	0.03
Materials giving soft tannage—			
Mangrove (*Rhizophora mucronata*) bark	10.31	23.42	0.26
Gambier, 1st sample	12.42	*42.48 †16.40 (58.88)	0.82
Gambier, 2nd sample	13.0	—	1.58
Oak (*Quercus incana*) bark	9.3	13.94	0.26
Babul (*Acacia arabica*) bark	10.20	11.17	0.36
Do. do. pods	9.80	16.96	0.42
Cassia auriculata	10.8	16.86	1.08
Myrobalans	8.75	51.69	0.25

* Catechin. † Tannin.

It is thus seen that the tan barks which are known to give

* *J. S. C. I.*, March 15, 1915, pp. 208-9.

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harsh tannage contain less fatty matter than those giving soft tannage, nevertheless the ability of certain tanning materials to give soft tannage may be influenced by several factors, of which fat may be only one. Whether the fat in the bark has any influence on the hide during tanning can be gathered by observing whether the fat emulsified into the tan liquor gets absorbed by the leather, and whether the hide when partially tanned and kept in prolonged contact with bark actually absorbs fat from the finely powdered tanning materials in contact. Repeated extraction with water does not remove fat from the bark. The following table gives the fat contents of the materials mentioned above when their tannin has been removed by repeated extraction with water, and after drying the residue and extracting it with petroleum spirit. The results are in fair agreement with those obtained by direct extraction with petroleum spirit, but in some cases there is a slight increase, which may be due to the elimination of tannin. It seems that the fat occurring in the barks is not emulsified with water and so there is no likelihood of its being absorbed from the water extract by the hide. An additional proof is afforded by the mangrove extract. It gave to petroleum spirit only 0.03 per cent., which shows that in the process of tannin extraction, the fat is not extracted by water from the barks.

No.	Name	Moisture Per cent.	Fat Per cent.
1	Sal bark	10.60	0.19
2	*Terminalia tomentosa* bark	6.70	0.20
3	Mangrove bark	11.70	0.39
4	Oak bark	9.30	0.39
5	Myrobalans	9.40	0.19
6	Babul bark	10.20	0.32
7	*Cassia auriculata*	10.80	0.82

The absorption of the fat by the hide during tanning is quite evident in the case of gambier. The fat in the gambier becomes suspended in water when the material is dissolved, and is absorbed by the hide along with tannin. This fact is supported by the experiments of Garelli and Apostolo (*J. S. C. I.*, 1913, 877; this J., 1913, pp. 414-15), showing that insoluble fatty acids simply suspended in water are fixed by skin and tan just as efficiently as when dissolved in alcohol or emulsified in water with ammonium soaps.

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The fact that gambier yields soft tannage may be due to its fat content. Experiments were made to see if fat is similarly absorbed by the hide from various other materials. Small pieces of hide (8 grams) were freed as far as possible from superficial fat by repeated extraction with petroleum spirit and then kept for about 40 days in contact with fine powder of different tanning materials in quantities calculated to contain 2 grams of tannin. The results are tabulated below:

Material	Quantity of the tanning material taken grams.	Petroleum spirit solubles in the tanning materials taken per cent.	Total fat in the leather obtained per cent.	Net amount of fat absorbed per cent.	Percentage of fat absorbed out of total petroleum spirit extract.
Mangrove extract.....	3	0.0009	0.017	Nil	Nil
Sal bark	12	0.0024	0.017	Nil	Nil
Terminalia tomentosa.	18	0.0324	0.018	0.001	2.7
Oak bark	14	0.0368	0.020	0.003	8.3
Babul bark	16	0.0576	0.027	0.010	17.4
Babul pods.....	10	0.0420	0.020	0.003	7.1
Cassia auriculata.....	11	0.1188	0.022	0.005	4.2
Mangrove bark.....	5	0.013	0.023	0.006	46.0
Control: pure tannic acid	2	—	0.017	—	—

These small scale experiments cannot be said to be conclusive, as a certain amount of experimental error is unavoidable. It will be seen, however, that the leathers absorbed more fat from the materials giving soft tannage than from those tanning harsh. The percentage of absorbed fat indicates the quality of the fats so far as their absorption by hide is concerned. These results indicate that the hide might in the prolonged process of tanning absorb fat direct from the barks, but it is difficult to say to what extent this absorption really takes place in the tan-pit. In the old process of tanning by contact with barks for several months, it is possible that the fat might have a softening action on the resulting leather. Whether the fat-content of the bark plays any part in the tan-pit or not, the co-occurrence of fat with such tanning materials as give soft tannage suggests that, possibly as the results of certain metabolic processes in the tree, the tannin accompanied by a certain quantity of fat has the property of giving soft tannage. On the other hand, myrobalans do not contain much fat and yet they tan soft.

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Suggested Addition of Fat to Tannin Extracts.

The above results suggested the addition of fat to tannin extracts of all kinds in order to reduce the harshness of tannage. Experiments were therefore carried out to see whether the addition of fat to tan-liquors made from solid tan extracts does actually influence the result. The simultaneous absorption of traces of fat along with tannin by hide cannot but be useful in giving soft leather of better texture, if the presence of fat does not retard the tanning process.

Six pieces of hide well-limed, washed, and cut into equal sizes of 12 inches by 6 inches, were put in stoppered bottles together with 1 liter each of the tan liquors (2 per cent. tannin) made from the solid tan extract of mangrove, sal bark, and myrobalans. In three bottles no fat was added and in the other three 10 per cent. of fat (oil of the seeds of *Schleichera trijuga*) calculated on the tannin content, was added, and all the six pieces were tanned under similar conditions. All the pieces took the same time to be struck through. They were then taken out, thoroughly washed till free from excess of tannin, dried in the shade, equally stretched, and finished off. They were not fat-liquored.

The results obtained are tabulated below:

No.	Name	Description of the leather obtained
1	Mangrove with fat	Softer and with better texture than No. 2.
2	Do. without fat	Hard though not cracky.
3	Sal with fat	Distinctly softer and with better texture than No. 4.
4	Do. without fat	Hard though not cracky.
5	Myrobalans with fat	Soft, hardly distinguishable from No. 6. Texture and surface feel better.
6	Do. without fat	Soft leather.

It will be seen that an addition of fat to the tan-liquors made from the extract improves the leather without retarding the process of tanning, and that the simultaneous absorption of traces of fat along with tannin, by the hide softens the resulting leather; this effect on the texture of the leather cannot be produced by subsequent fat-liquoring. It seems that the property of tannin extracts which give harsh tannage is somewhat mellowed down. Moreover, the addition of fat would have a protective action on tannin and thus avoid to a great extent the loss of tannin that

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takes place in tannin extracts on storage. It is therefore suggested that trials should be made in this direction by manufacturers of tannin extracts. Even in case of extracts of such materials as myrobalans, it is preferable to add fat which will have a protective action on tannin, irrespective of the question of the softening action.

The oils and fats ordinarily used for fat-liquoring could be used for the purpose, but it is preferable to have a mixture of oil and fat of the consistence of treacle. About 10 per cent. of fat calculated on the tannin content should be added to the vacuum pan, where it should get thoroughly emulsified with the tan-liquors. This fat will be available in a partly emulsified form when the solid extract is made into liquor in the tan-pit or the tanning drum.

Discussion.

In reply to questions, the Chairman said that hitherto fat had always been applied to thick leathers, such as hides, by currying; in this process the dry skin was immersed in melted fat, or the fat was put on the surface of the moist leather and allowed to penetrate slowly. "Fat-liquoring" was applied to light leathers immediately after tanning: neatsfoot oil was used for the purpose. The addition of fat to the extract in the drum during the tanning process was practiced already in certain cases.

Professor Procter wrote that the paper was interesting and the idea of using oil appeared practical, though not quite new, especially in drum tannage. He thought drumming with a fat emulsion (sulphated oils) and an extract might also give a very good "raw hide" leather.

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THE ANALYSIS OF GUARA AND GUARA EXTRACT.*

By Thomas Callan, M.Sc., Ph.D.

Guara is a newly-introduced tanning material which, according to Eitner (Gerber, 1914, 40, 85—86) is identical with a material introduced 25 years ago under the name of Cascalotte. It was thought to be of interest to compare the material offered to British tanners as "guara" with the material described by Eitner. According to Eitner guara consists of the ground fruits of a variety of divi native to South and Central America, freed from seeds and woody husks. In agreement with this the samples of guara examined were found on microscopical examinations to consist almost wholly of fruit wall minus the outer husk. The most distinctive features in the microscopical appearance are the small brown plates showing a honeycomb structure and small brown plates furnished with stiff needle-shaped hairs, probably portions of outer epidermis and underlying tissue. According to Eitner (*loc. cit.*), guara contains a mixture of pyrogallol- and catechol-tannins, but practically all the reactions of guara tannin were found to agree with a pyrogallol-tannin closely resembling the tannins of sumach or myrobalans. Thus a dilute aqueous infusion of guara gives a violet-blue coloration with iron alum, no precipitate with bromine water, no phloroglucinol reaction with a deal shaving, a yellow precipitate turning green with lime water, a slight precipitate with formaldehyde and hydrochloric acid, a yellow coloration with sodium sulphite, an intense red or brownish-red coloration with an ammoniacal solution of potassium ferricyanide in very dilute solution, a pink to purple coloration with Bennett's iodine test, and a deep orange-brown color with nitrous acid. With concentrated sulphuric acid, however, a crimson-pink coloration changing to pink on dilution is obtained—a reaction given by most catechol-tannins.

A number of analyses of various samples of guara made during the past 2 years show that material of a remarkably constant quality is being supplied. The following are typical analyses, carried out according to the official method of the International Association of Leather Trades Chemists:

* *J. S. C. I.*, June 30, p. 645.

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	Tans per cent.	Non-tans per cent.	Insoluble per cent.	Moisture per cent.
1.	43.5	23.8	22.0	10.7
2.	46.2	25.8	19.0	9.0
3.	48.4	23.2	17.7	10.7
4.	44.8	23.1	21.7	10.4

Mr. H. Long, of the Gryfe Tannery, Ltd., kindly carried out for me a number of tanning experiments with guara and also made trials of this material on the large scale in conjunction with other tanning materials. According to these experiments, skins tanned entirely with guara gave a soft well-filled leather, resembling a gambier tannage rather than a sumac or myrobalan tannage such as the presence of pyrogallol-tannins might lead one to expect. The well-nourished appearance of guara-tanned leather may, therefore, be largely due to the nature of the non-tannins present.

Guara is quite free from the liability to give excessive fermentation such as is characteristic of divi. However, its fine state of sub-division prevents guara from being readily leached, although the tanning matters are very readily soluble. Guara has been found excellent for developing acidity in the tan-liquors, and when used with untreated quebracho extract has a very favorable influence on the color of the leather. It has been found particularly useful mixed with quebracho extract in the paddle, as it does not draw the grain but gives a soft and mellow tannage. The most characteristic features of guara are its acid-forming properties and the light color and mellowness of the tannage.

Guara Extract. Only one sample of guara extract (solid) has been examined, as this material is no longer imported.

The analysis gave tans, 41.7 per cent.; non-tans, 30.0 per cent.; insoluble, 11.0 per cent.; moisture ,17.3 per cent., agreeing closely with the analysis given by Eitner. Guara extract gives a very dark colored infusion and besides being actually weaker in tannin, is inferior in all respects to the natural product. The large amount of insoluble matter makes its filtration during analysis very difficult. It is reported by Eitner to make a dark-colored and unsatisfactory leather, and as it has not been favorably received by British tanners it is no longer imported.

NOTE ON THE ANALYSIS OF TANNING MATERIALS.

Whilst the experiments on guara described above were in prog-

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ress there appeared a paper by H. G. Bennett (*J. S. C. I.*, 1914, 1182—1184) in which a modified method of tannin analysis was proposed.

Briefly stated, Bennett proposes to modify the present official method of the International Association of Leather Trades Chemists by (1) exactly neutralizing the hide powder before the preliminary chroming, (2) using less hide powder, (3) diluting the solution to be detannized with an equal volume of water, (4) using a more basic chromium salt for chroming. The object of these modifications is to obtain lower tannin results and higher non-tannins, this being a step towards greater accuracy, as the chief objection to the present method is that the hide powder absorbs small quantities of non-tannins as well as tannins. To test this new method analyses were made of guara using (1) the present official method with American hide powder of standard quality, (2) Bennett's method using American standard hide powder, (3) Bennett's method using finely ground hide powder obtained from the Deutsche Versuchsanstalt für Lederindustrie, Freiberg. Using the same tannin solution, the amount of non-tannins obtained by these three methods were, to give only one example, 23.1 per cent., 28.1 per cent., and 25.4 per cent. respectively. Repeat experiments gave similar results.

In each case 50 cc. of the detannized filtrate was tested by the official test for tannin (the addition drop by drop of a 1 per cent. gelatine 10 per cent. salt solution) when no turbidity or opalescence was obtained, indicating apparent complete detannization. This would indicate that the most accurate result was No. 2 showing the least absorption of non-tannins. The correctness of this reasoning, however, depends entirely on the trustworthiness of the official gelatine salt test. The non-tannin filtrates were, therefore, retested by the tannin test devised by Stiasny, which consists of adding 1 cc. of a saturated salt solution, then 2 drops of 1 per cent. metaphosphoric acid solution and finally 2 drops of 5 per cent. gelatine 5 per cent. salt solution to 3 cc. of the solution to be tested. With this more sensitive test No. 1 and No. 3 showed no tannin, whilst No. 2 showed a distinct trace. The dried non-tannin residues after weighing were therefore dissolved in 15 cc. of warm distilled water, filtered and 3 cc. tested by

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Stiasny's test. No. 1 gave no reaction, No. 2 gave a heavy precipitate, whilst No. 3 gave a distinct opalescence, indicating a slight trace of tannin. From these experiments with guara, which were repeated several times with similar results, the only method showing perfect detannization is the present official process, although the amount of tannin remaining unabsorbed in Bennett's method when the finely ground Freiberg powder is used, is very small. Although the present official method undoubtedly detannizes very completely, this does not mean that it is the more accurate, as these experiments do not show how much non-tannin is also absorbed. A number of experiments were then made to determine the approximate degree of accuracy of the present official tannin test. With a solution of guara and also of chestnut extract it was found that 50 cc. containing 10 milligrams of tannin gave a distinct reaction, whilst 6.5 milligrams in 50 cc. could not be detected, although Stiasny's test readily showed as little as 3 milligrams in 50 cc. when only 3 cc. of solution was taken for the test. With quebracho extract the official test is more delicate indicating distinctly 5 milligrams but not 2.5 milligrams of tannin in 50 cc. It follows, therefore, that a solution apparently completely detannized when tested by the official method may still contain, with some tanning materials, up to 6.5 milligrams of tannin in 50 cc. This would correspond in the case of a tanning material containing about 50 per cent. tannin to nearly 2 per cent. tannin, whilst with Bennett's method, owing to increased dilution, it corresponds to about double this amount. Before conclusions as to the relative efficiency of different methods of detannizing tannin solutions can be drawn, it is, therefore, necessary that a more stringent test than the present official tannin test be used. A sufficiently stringent test would be to concentrate 6 cc. of the presumably detannized solution (or 12 cc. if Bennett's method or other method involving solutions more dilute than the present limits be used) to 3 cc. and apply Stiasny's test.

In the course of a number of analyses of various tanning materials it was found, as in the case of guara, that the non-tannin filtrates obtained in Bennett's method, using standard American hide powder, showed in many, though not all, cases distinct traces

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of tannin, even after shaking 20 minutes with hide powder, when tested by the more sensitive method after concentration, although no tannin was shown by the official test. It would appear, therefore, that the alteration in the various factors in this method, designed to reduce absorption of non-tannins, has been carried too far and although in all probability the gain in accuracy owing to reduced absorption of non-tans is more than the error introduced by the non-absorption of traces of tannin, the presence of this latter error will probably prove a strong objection to the method as it now stands.

In conclusion it may be noted that although Stiasny's test will give a positive reaction with gallic acid in sufficiently concentrated solution, it will not show 150 milligrams of gallic acid in 50 cc., which is about the maximum amount of gallic acid likely to be pesent in a detannized solution even after concentrating to half its volume.

A SIMPLE INSTRUMENT FOR THE DETERMINATION OF VISCOSITY.*

By Alan Speedy.

In the determination of viscosity by the aid of viscosimeters of the Ostwald type, it is customary to immerse the whole apparatus in a medium of high boiling point. The use of a fairly large quantity of some oil or wax transparent at the temperature of observation is thereby necessitated.

In the simple instrument described below, all difficulty in reading the marks is avoided by placing them above the surface of the liquid, which, therefore, need not be transparent and of which only a moderate quantity is required.

The instrument consists of a piece of glass tubing drawn out to form a capillary and bent into U shape, as shown in the figure.

The liquid of which the viscosity is to be determined is filtered into the viscosimeter, which is clamped vertically in the bath so that the level marks, a, a', are just above the surface of the heating liquid. The bath is now heated to the required temperature

**J. S. C. I.*, June 15. pp. 597-8.

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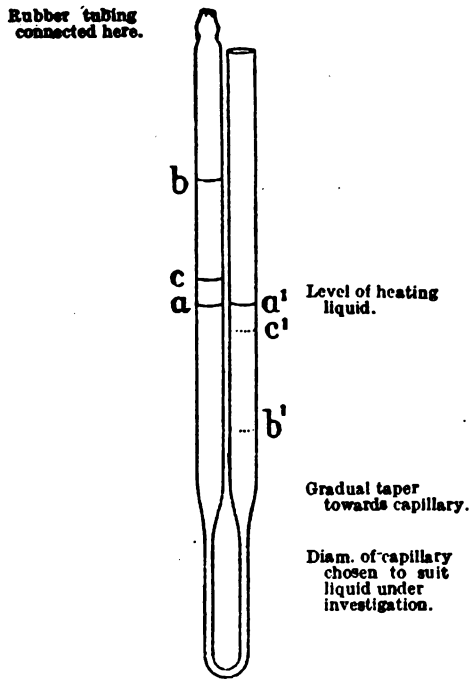
and after a few minutes the levels, a, a', are carefully adjusted. By means of a piece of rubber tubing the liquid is then slowly sucked up the left limb of the tube until it passes the level, b. It is then allowed to descend. The time taken to fall from b to c is recorded on a stop watch, and the experiment repeated as a check.



Two-thirds scale.

Part of the liquid under observation is above the surface of the heating liquid and is, therefore, at a slightly lower temperature, but as the level falls, this part of the liquid regains its former temperature. The error due to unequal viscosity in different regions arising in this way is negligible. It is only the viscosity of the liquid in the capillary tube that counts. The thinness of the wall of the capillary tube ensures that the liquid passing through the tube is at the temperature of the bath. It should be observed that the column of liquid, bc, never reaches the capillary. The level, b', is well above the point where the

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constriction in the right limb of the tube begins. The time of flow is taken from *b* to *c* only, because on approaching *a* the motion becomes slow and uncertain.

The constant of the instrument can be obtained by calibrating it with pure phenol (see A. E. Dunstan, *J. S. C. I.*, 1912, 31, 1063) or sulphuric acid (see *Proc. Chem. Soc.*, 1914, Vol. 80).

The instrument may conveniently be strapped to a thermometer and suspended in the heating liquid, which is contained in a boiling tube. The cheapness of the apparatus renders it possible to choose from a range of tubes, one with a capillary of diameter best suited to the viscosity of the liquid which is to be investigated. The best results are obtained if the time of flow is about 1-2 minutes at the temperature of observation.

As an illustration of the degree of accuracy that may be expected from this form of viscosimeter, the examples contained in the table below are given.

Sample	Nominal Sp. gr.	T°	η Dunstan	η New type	Secs. Redwood	Closed flash pt. °F.
Genuine refined pale East Indian rape oil	0.910	60° F.	—	—	535	
		70° F.	0.7680	0.7669	312	
		140° F.	0.1864	0.1872	98	
		200° F.	0.0815	0.0818	55	
American pale oil A	0.900	70° F.	0.7600	0.7592	348	
		140° F.	0.1230	0.1224	69	390
		200° F.	0.0497	0.0495	41	
		250° F.	0.0283	0.0283	34	
American pale oil B	0.908	70° F.	—	—	490	
		140° F.	0.1580	0.1575	80	
		200° F.	0.0583	0.0578	45	400
		250° F.	0.0328	0.0327	36	
Russian pale oil	0.908	70° F.	—	—	1235	
		140° F.	0.2624	0.2611	134	384
		200° F.	0.0853	0.0859	53	
		250° F.	0.0421	0.0423	40	
Neptune brand lubricating oil	0.850	150° C.	0.0718	0.0714		
		180° C.	0 0450	0.0452		
		200° C.	0.0348	0.0355		
Shale oil distillate	0.840 to 0.860	40° C.	0.0316	0.0319		
		80° C.	0.0145	0.0149		
		100° C.	0.0114	0.0117		

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Six oils, of which five were kindly supplied by Messrs. Ragosine & Co., were tested for viscosity in the instrument just described, and also, for the sake of comparison, in two other forms of viscosimeter, of which one is the totally immersed type,* and the other the well-known Redwood form.

The readings of the first two instruments agree within the limits of experimental error. At 140° F. it will be seen that Redwood seconds may be obtained approximately by multiplying these readings by 500.

It is believed that the extreme simplicity of the instrument, and the increased accuracy due to choice of a suitable capillary, as well as its convenience in use, may recommend it to all who have measurements of viscosity to make.

ABSTRACTS.

The Concentration of Sewage Sludge. J. GROSSMAN. *J. S. C. I.*, June 15, pp. 588-92. In general, settling tanks produce a sludge containing about 10 per cent. solids. It is important where sludge is to be transported, to reduce the water content. To produce a cake containing 30 per cent. dry material costs about 56 cents per ton when lime is used. Filter-pressing without lime is more difficult and expensive. For many purposes to which sludge is applied, the presence of lime is objectionable. The cost of drying sludge containing 5 per cent. solids is about $7.50 per ton of dry matter with coal at $2.50 per ton. If the solids are 10 per cent., the cost is $3.75, a difference of $3.75. A 30 per cent. sludge costs 94 cents per ton of dry matter, and a 35 per cent. sludge 74 cents, a difference of only 20 cents. The author concludes that if sludge is to be dried by heat it is not worth while to concentrate by mechanical means beyond 30 per cent., and that anything beyond 20 per cent. could be dried economically. In the effort to develop a method of concentrating sludge up to 20 per cent., the author tried a settling tank connected with a filtering compartment, the sludge being removed by a conveyor screw. The degree of concentration by this method approached 20 per cent., but the time consumed was too great, and the sludge was partly decomposed, causing lack of uniformity and consequent trouble in the driers. A method devised by the author and now in use for a year at the Oldham Corporation Sewage Works, handling the sludge from a city of 150,000 people, employs sulphuric acid of 10 per cent. strength, which is added to a 10 per cent. sludge in the proportion of 3 parts per 100 and the mixture is then allowed to stand 3 days. The concentrated material floats, so that the liquid (now nearly neutralized) is drawn off at the bottom. The original sludge varies from 10 to 13 per cent. and the concentrate from

* A. E. Dunstan, *ibid.*

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19 to 21 per cent. The total cost of the process per ton of dry matter is 50 cents, half of which is for sulphuric acid. By slightly varying the process a 30 per cent. sludge may be obtained, but this offers no special advantages for subsequent drying. The cost of producing 1 ton of dry matter by filter-pressing and drying is about $5, while by the sulphuric acid concentration and drying it is only $1.75. Dried sludge has a considerable value as a "base" for fertilizers.

The Constants of the Fatty Acids from Sulphonated Cod Oil. L. G. RADCLIFFE and C. W. PALMER. *J. S. C. I.*, June 30, pp. 643-4. A brown cod oil, sp. gr. 0.931, saponification value 16.33, acid value 17.6, iodine value 173.7, was saponified with a strong solution of potash to which alcohol had been added, the soap boiled with water to remove the alcohol, and the fatty acids separated by means of hydrochloric acid. The acids were washed with water, and after separation heated to remove traces of moisture. The solidifying point was 22.8° C., neutralization value 194, mean molecular weight 289.4, iodine value 178, yield of hexabromides 42 per cent. One hundred grams of the oil was sulphonated in a water-cooled vessel by adding 35 grams of sulphuric acid drop by drop, with continual stirring. The temperature at no time exceeded 25° C. No SO_2 escaped. The dark thick product (after 2 hours' stirring) was washed with a cold saturated solution of sodium sulphate until nearly all free sulphuric acid was removed. The resulting oil was saponified in the same manner as the original cod oil, and the fatty acids liberated. They contained no sulphur. The solidifying point was 25.7° C., neutralization value 183, mean molecular weight 308.6, iodine value 114.4, yield of hexabromides 11.0 per cent., indicating an extensive change in the character of the fatty acids during the process of sulphonation.

Tree Dyes of the United States. *Hardwood Record*, May 25, 1915. The war has cut off the supply of aniline dyes which formerly came from Germany to the United States. Some of the colors have become wholly exhausted, and others will last from 1 to 2 months. There is no present prospect of others being imported. Some steps have been taken toward building up a coal tar dye industry in this country, but the fruition of the plans lies a long way in the future. The situation will soon be acute. Of course, we can live without dyestuff, but no nation, either savage or civilized, ever did it.

America can fall back upon its own resources, but there may come a time soon when certain of our neglected forest supplies will be drawn upon. They were used once. Before coal dyes were invented, the people peeled bark, dug roots, chipped wood and made dyes. The colors were not so brilliant as the aniline dyes; but some people prefer colors not too brilliant. The subdued tones of genuine oriental rugs are not dissimilar to what might be produced from the bark and wood of certain American forest trees. The people have almost forgotten what our forests contain in the way of coloring matter.

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A government commerce report, issued by the Department of Commerce, recently discussed the dye situation very fully, except that the report was somewhat lame concerning the resources of our forests in dyestuffs. It was stated that the black oak (*Quercus nigra*) is the source of "the only natural dyestuff indigenous to the United States." It is a mistake in name, for it is the yellow oak (*Quercus velutina*) and not the black oak (*Quercus nigra*) that supplies the quercitron for dyeing purposes. The yellow oak has a much wider range than the black oak, and is also more abundant.

The government report above mentioned is entirely too modest in allowing that yellow oak is our only source of tree dye in this country. There are many others. The pioneers knew them by the dozen. Those people understood nothing about chemistry, but they learned by experience that certain barks would dye cloth, yarn, wool and leather. Following are a few native trees whose wood, bark, roots and fruit have been employed for dyeing.

First of all is yellow oak. It ranges from Maine to Minnesota and southward to Florida and Texas. It covers a million square miles. The coloring matter lies in a thin layer under the bark, being a part of the inner bark.

Butternut (*Juglans cinera*) was formerly a valuable dye material. It usually colored brown, but the shades could be varied. The "Confederate jeans," the cloth much used for Confederate uniform in Tennessee and Kentucky during the Civil War, was dyed with the bark of this tree. It was not the historic "Confederate gray." The tree is found in all northern states east of the Mississippi River, and even westward, and it grows also in most of the southern states.

Black walnut (*Juglans nigra*) furnished dyes from the outer hulls of the nuts. The color was slightly darker than that produced by butternut bark, and was not so popular.

Osage orange (*Toxylon pomiferum*) was limited in its original range to about 10,000 square miles of northern Texas and southern Oklahoma, consequently it was not widely known to early settlers; but the roots, bark and wood produce a fine yellow dye that has been compared with fustic.

Yellow wood (*Cladrastis lutea*) yields a yellow dye, to which the wood owes its name. The tree is confined to Kentucky, Tennessee, Alabama and North Carolina, and is nowhere abundant. The homespun of the pioneers was occasionally colored with this dye.

Mesquite (*Prosopis juliflora*) furnished dyes with which the Spanish horsemen of Texas, New Mexico, Arizona and southern California imparted the yellow colors to saddle leather.

Staghorn sumac (*Rhus hirta*) supplied a dye for coloring fine leather, as well as the tannin for dressing it. The dye was yellow and was occasionally employed in coloring cloth.

Alder (*Alnus sp.*) appears not to have been used in America by any

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people except the Indians. It dyes a reddish color, and down to a few years ago was employed by natives of the northwest Pacific coast in coloring their fish-nets. Alder dye used for the same purpose is said to be the oldest recorded dye in the world. It is mentioned in the *Kalevala* of Finland, supposed to date nearly 3,000 years ago.

Red gum (*Liquidambar styraciflua*) was used by the early Swedish settlers of Pennsylvania and New Jersey in dyeing purple, but the secret of the process seems to have been lost.

Locust (*Robinia pseudacacia*) is said to possess possibilities in the way of dyes, but authenticated records of its use appear not to be at hand. A very similar tree of China supplies the brilliant yellow dye so admired in China silks.

Bluewood (*Condalia obovata*) is found in the valley of the Rio Grande in Texas, where the largest trees are 30 feet high and 6 or 8 inches in diameter. It is known also as logwood because of its resemblance to the dyewood of that name in tropical America. Locally, a black dye is obtained by boiling the finely chipped heartwood. There is no account that it has ever been used commercially.

Dogwood (*Cornus florida*) was the source of the famous "Indian red" with which the vain warriors dyed their eagle feathers and buckskin clothes. They procured the dye from the roots of dogwood. They used in the same way the roots of western dogwood (*Cornus nuttallii*). This is probably the most brilliant dye to be procured from American trees.

Influence of the Method of Subdivision of Leather on the Results of Analysis. R. LAUFFMANN. *Ledertech. Rundschau*, May 22, pp. 161-4. Leather ground in steel mills is likely to be contaminated by particles of iron, on which the acids of the leather may react. That the water content of ground leather is different from that of the original sample or from a cut up sample, is well known. Since the other results depend on the water content, analyses of the same sample are only comparable when they have been calculated to the same water content. The Leather Analysis Commission has assigned 18 per cent. as the average water content of unstuffed leathers. The moisture in leathers containing fat depends on the fat content. Since both the fat and the water soluble must be extracted from the leather, it seems evident that they also will depend to some extent on the mode of division. Results on the fat content of the Commission's samples are as follows:

FAT.

Leather No.	I.		II.		III.
Solvent	Carbon disulphide Per cent.	Trichlor-ethylene Per cent.	Carbon disulphide Per cent.	Trichlor-ethylene Per cent.	Carbon disulphide Per cent.
Ground	1 9	1.6	17.8	16.8	21.1
Cut	2.0	2.0	17.3	16.2	20.9

The author supposes that a reason for lower results in the case of a ground leather may be the combination of fatty acids with iron par-

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ticles, forming insoluble compounds and thus escaping detection. The organic water soluble figures from the same three samples were found by leaching in Koch's apparatus at 40° C. and also by shaking out with a measured quantity of water at room temperature, as shown in the table:

WATER-SOLUBLE.

Leather	I.		II.		III.	
	Koch's flask Per cent.	Shake method Per cent.	Koch's flask Per cent.	Shake method Per cent.	Koch's flask Per cent	Shake method Per cent.
Ground	11.2	7.4	11.6	10.9	4.0	4.2
Cut	6.0	5.6	9.3	10.2	3.6	3.7

The higher figures for the ground leather consisted chiefly of tannin, the non-tannins being about the same in the two cases. This difference is important, since it affects the tannage number. The total mineral matter in sample I ground was 0.8 per cent., of which 0.26 per cent. was oxides of iron and aluminum, while in the same sample cut the whole mineral content was 0.6 per cent., of which 0.19 per cent. consisted of iron and aluminum oxides. The nitrogen figures were the same for ground and cut samples. The difference in content of free acid, especially sulphuric, was very marked.

SULPHURIC ACID.

	Balland and Maljean or Paessler and Sluyter		Rehbein
	Total SO_3 Per cent.	Free SO_3 Per cent.	Free SO_3 Per cent.
Sample I ground	1.07	0.23	0.29
	1.03	0.19	0.23
Mean	1.05	0.21	0.26
Sample I cut	1.23	0.54	0.39
	1.24	0.55	0.39
Mean	1.24	0.55	0.39

The author assumes that this difference in free acid is due to the iron from the mill combining with the acid of the leather. As has already been stated by the author (see abstract, p. 330, June issue, this J.) the Procter-Hirst test and the Appelius test for cellulose in leathers are much less pronounced in the case of ground than in the case of cut samples. The conclusion is that a uniform method of division of leather samples for analysis must be adopted, and that the division must be by cutting and not grinding. L. B.

Analysis of Turkey Red Oil. M. HERBIG. Abstract by A. L. in *Le Matieres Grasses,* May, 1915, p. 4316. In order to separate the neutral fat of turkey red oil, the sodium salts, and the free fatty acids, M. Herbig prescribes the following method. The water content is determined by heating in a platinum dish. Depending on the amount of water, from 2 to 5 grams of the oil are weighed out in a platinum dish, dissolved in

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water and exactly neutralized to phenolphthalein by N/1 or N/10 NaOH. Most of the water is now evaporated on a water bath, and the rest expelled over a free flame. The end-point is easily recognized after a little practice, and it is important not to pass it. The saline mass is boiled four times with 75 cc. of anhydrous acetone on an air bath, the material being broken up with a glass rod. It is now cooled to 0° C., with constant agitation, then allowed to settle, and the liquid decanted through a filter into a flask, as little as possible of the undissolved matter being allowed to pass onto the filter (often a process of some difficulty). Most of the acetone is now driven off, and the residue transferred with the aid of a little fresh acetone to a platinum dish, which is heated on a water bath with agitation until the odor of acetone ceases and the weight becomes constant. The residue is dissolved in alcohol and ether and serves for the determination of the acid value and the saponification value. The salts remaining in the first mentioned platinum dish and on the filter are easily dissolved in cold water. The portion on the filter is washed into the dish with a little cold water and a glass rod. This water solution is slightly yellow ("Monopole" soap) and froths much when shaken. The solution is now decomposed with boiling HCl in a large Erlenmeyer flask, the combined sulphuric acid being thus separated. The decomposition is complete when the melted fatty acids separate in a clear layer, and the acid solution is but slightly turbid. The mass is now cooled and transferred to a separatory funnel with the aid of some ether and water, extracted with ether, and the ethereal solution washed three times, each time with 10 cc. of water. The water solution is heated to expel ether, and the sulphuric acid precipitated with barium chloride in the usual manner. The ether from the ethereal solution is allowed to evaporate, and the fatty acids transferred to a small beaker, when they are dried over a small flame, weighed, and then used to determine the acid value and saponification value. The total SO_3 in the original turkey red oil is greater than the amount found by this process, since some of the sulphur compounds dissolve in the acetone, from which it is possible to recover them. The examination of four products has given the following results: (1) The saponification value of the total fat separated by HCl corresponds well, in the four experiments, with the saponification values determined on the original oil, and proportional to the anhydrous oil. (2) The acid value of the total separated fat is sensibly the same (134 to 140) in the four cases. The acid value of the fatty acids, prepared by means of the fatty salts isolated by the acetone process, are also almost identical (155 to 160) for three commercial products essentially different, "Monopole soap," "Turkone N oil" and ordinary turkey red oil. (3) There is not much difference in the combined SO_3 of these three distinct oils. This fact is remarkable. (4) The ratio of acetone extract to fatty acid for the three materials is as follows: Monopole soap, 1.13; Turkone N, 1.45; ordinary turkey red, 1.78. This ratio, together with the moisture, the saponification value of the original sample, the total fat and the ratio of combined sulphuric acid to anhydrous oil, give.

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an indication of the constitution of the oil, and permit a valuation of the different products. The determination of water, which may easily be done in ½ hour, gives an approximate value for total fat, since water plus fat equals about 90 per cent. In most practical cases this experiment is sufficient. The acetone process permits the almost quantitative separation of the constituents of turkey red oils in a short time and with no great difficulty. For Monopole soap and similar products, decomposition with hot HCl separates SO_3 quantitatively, boiling 1 or 2 minutes in an open flask and repeating two or three times. L. B.

Gambier. *Hide and Leather*, May 29, 1915. The director of the Government Laboratory at Buitenzorg (Java) has contributed an article to the Holland Department of Agriculture, Industry and Commerce on gambier. The leaves of the plant contain the tannin, which is extracted in concentrated form by boiling in a cast iron (?) pan on an open fire. Equal weights of water and leaves are used. The Chinese gambier boilers pour boiling water several times on the leaves and the weakest residue liquor is used for the next batch. Much gambier is produced in a primitive and wasteful manner at comparatively high cost. Factories using modern methods and proper equipment get richer tannin at lower cost. It would be well if more gambier were produced scientifically, as it is one of the most valuable of tanning materials. Sometimes the extract is poured into moulds, and, after being dried in the sun, is ready for market. It is somewhat sticky, but contains the highest percentage of tannin. Mixed with chrome or alum, gambier gives a beautiful color to leather. It is used all over the world, owing to its high percentage of tannin. Cube gambier contains between 55 and 63 per cent. of tannin. Block gambier usually has about 40 per cent. tannin. As high as 50 per cent., however, is stated to be in the block gambier produced by the Goonoong Malajoe Plantation Company of Zurich, Switzerland. This enterprising corporation has its factory at Asahan, Sumatra, Dutch Indies, and is said to be the only plant there producing gambier in a thoroughly modern and scientific manner. Gambier is a most valuable tanning material. Carefully and skillfully used, it produces a beautiful, soft, supple, cream colored leather. If used too strong, however, gambier makes leather brittle; hence the importance of thoroughly understanding the penetration qualities of the material. In combination tannages gambier is very successful. Gambier has the advantage of being obtainable all the year round. Large quantities are produced in the Dutch Indies. Unless purchased, however, from honest and reliable producers, gambier is liable to be badly adulterated. For this reason tanners usually employ chemists to supervise their purchases.

Tanning Industry of the Philippines. *Commerce Reports*, J. F. Boomer, Correspondent, Manila, May 22. An effort is being made to stimulate and develop the leather industry in the Philippine Islands. It is estimated that the producers and tanners of hides could save $350,000

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annually by investing but little more capital than is now employed, simply by adopting modern methods. It is estimated that about 18,000 skins are tanned annually in the islands. The leather produced is manufactured into slippers and shoes of the lower grades. The value put upon this annual output of the tanneries is about $150,000. There are many skins—from deer, wild hogs, etc.—of which no use whatever is made. The 125 tanneries are scattered through the various provinces. Those of most importance are in Manila, Iloilo, Bulacan, Ilocos Norte, and Ilocos Sur. The tanning is poorly done and from poorly selected skins. As a result, thick skins for making hard, thick sole leather come from the tanner flexible and incompletely tanned, through the use of weak tanning solutions and insufficient time in the tanks or vats. Not infrequently these leathers are not sufficiently tanned to prevent decomposition. At best such leathers are of light weight and porous and flexible. The Bureau of Science recommends that 4 months be devoted to the tanning process. The process proposed is to immerse the skins first in a solution containing about one-half of 1 per cent. of tannin and pass them gradually to baths of stronger solutions, the last solutions containing 10 to 15 per cent. of tannin. The present practice is generally to immerse the skins in a strong solution at first and allow them to remain only 4 to 6 weeks. The result is preserved skins rather than leather. The Philippines are rich in tanning materials, which, properly employed, would make locally produced leather not only of the highest class but also cheaper than that produced elsewhere. The mangroves, which abound in different parts of the islands, and the camanchile tree (*Pithecolobium dulce,* a Mexican tree, having edible pods and a bark rich in tannin; introduced from Mexico into the Philippines and Guam), which grows in great abundance in the Philippines, furnish a large percentage of tannin. The fresh bark of these contains often 15 to 25 per cent. tannin, but as a rule no more than 10 per cent. is utilized. The cost of 100 kilos (220.46 pounds) of camanchile bark is $6; about $2.50 to $3 of bark is needed to tan a hide that in finished form should be worth $15, but because of its poor quality the leather turned out is worth only about $10. Investigation of the present system reveals great wastage. In one tannery 1,500,000 pounds of bark was used, but it was found that only 40 per cent. of the tannin was utilized. Again, a poor quality of lime is used for depilation, and care is not exercised in the washing process. The tanned product is dried too rapidly; the thick skins are divided until they are fragile and more or less valueless. The Government is endeavoring to reform the tanning methods and also to create marketing facilities for handling all the available hides of the islands. A propaganda has been started by the Bureau of Science to induce small dealers in remote communities to purchase hides from producers with the assurance that they will find a ready market at Philippine tanneries. By teaching the tanneries the latest methods it is hoped to stimulate a keener interest in the industry and encourage them to expand. An insignificant amount of hides has been exported during the last few years. In 1914, 23,486 pounds of carabao hides were exported

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to the British East Indies and Hongkong and 101,435 pounds, valued at $9,047, of hides of all other classes, principally to China and Hongkong, although small amounts were shipped to British East Indies, the United Kingdom, and the United States. This represents the high water mark of hide exportation in the last few years. During the 9 years from 1905 to 1914 the importations of leather and all manufactures of leather have increased from $536,559 to $1,557,824.

Vegetable Tanning Materials in 1914. J. JEDLICKA. *Gerber*, June 1 and July 1, 1915. In France an effort was made to have leather made entirely with oak bark prescribed for naval and military supplies (see this J., 1914, p. 194). Only a small fraction of the whole amount of tannin used in Europe can be furnished by oak bark. The rapid using up of the supply of chestnut wood available for the manufacture of extract is a serious question in France. A government commission on the subject is under appointment. R. Rieder has proposed using pine twigs for the production of extract (see this J., p. 107, Feb., 1915). Guara, from Brazil and Colombia, has come into the market (see p. 426, this issue). *Le Cuir* (1914, p. 135) discusses the causes of failure in the earlier efforts to cultivate canaigre, and anticipates good results in this line in the French African Colonies. Coombs and Dettman, in *Chemiker Zeitung*, write of the bark of the Australian fir, *Callitris calcarata*, with 21 per cent., and *Cal. glauca* with 12 per cent. tannin, of the catechol class. An English patent has been granted for the manufacture of an extract from *Erica scoparia* (leather), which is almost colorless. Lauffmann writes in *Rundschau* (see abstr., this J., July issue, p. 385) of new or little known materials. Oettinger published a monograph on new materials, including bodan roots, palmetto, cajotta bark, etc., with reactions, microscopic character, etc., and a bibliography. An English company is planning to make extract from wattle bark ("mimosa") in Natal. Some advances have been made in extract manufacture. Edmund Dammer, Duisburg, has obtained a patent for a decolorizing material obtained from the oil cake of soja beans. This product is called "edamin" (see abstr. this J., 1914, p. 271). A patent has been granted to the Wilsdorf Extract Works for a method of rendering soluble the "reds" of ordinary quebracho (German patent No. 36,999). The hot liquor is treated with materials of alkaline reaction, as the oxides, hydroxides or salts (carbonates) of the alkaline earths, in the absence of air, and then with the proper quantity of an acid which will form an insoluble salt with the alkali used. The Badische Corporation has patented a process for the same purpose, using the sodium salt of a condensation product of cresol-sulphonic acid and formaldehyde. The dissolving of solid extracts seems to offer practical difficulties, as a number of devices for this purpose have been patented during the year. A form of chestnut and oak extract has been put on the market which combines the advantage of liquid extract in ease of solution with a considerable saving of freight, less loss from leakage and no injury from freezing. This is a heavy liquid, about 40° Bé. L. B.

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The War and Scarcity of Tanning Materials. E. GLÜCKSMANN. *Gerber*, July 1. The writer details methods of using Neradol D; alone for light leathers, in combination for heavier leathers, and for bleaching purposes.

L. B.

PATENTS.

Process of Making Leather Materials. British Patent 1,401 (1914) and U. S. Patent 1,133,957. LEON HEIMANN, New York, Assignor to Live Leather Belt Co. The leather is crimped, stretched and rubberized.

Artificial Leather. U. S. Patent 1,140,174. LEON LILIENFELD, Vienna. A fabric coated with viscose, a phenol ester, etc., etc.

Leather Substitute. U. S. Patent 1,141,545. R. O. HERZOG, Prague, AND AUGUST MEIER, Berlin. A layer of micro-organisms is tanned.

Leather Manufacture. British Patent 5,863 (1914). Aluminum sulphite is used for reducing bichromate in a two-bath chrome process.

Leather Manufacture. British Patent 714 (1914). D. B. MACDONALD, Leicester. Leather is treated with a solution of viscose, celluloid, gun-cotton, or other material.

Process of Producing Soluble Tanning Agents. U. S. Patent 1,133,108. ERICH DENEL, Ludwigshafen, Assignor to Badische Company. Difficultly soluble tanning materials are treated with a condensation product obtained by acting on cresol with sulphuric acid and formaldehyde, which condensation product contains at least one hydroxyl group and at least one sulphonic acid group and is soluble in water, yielding an almost colorless solution which becomes deeply colored on the addition of a solution of a ferric salt.

Hide and Leather Working Machine. U. S. Patent 1,131,756. FRANCIS WAYLAND, Salem, Mass.

Leather Splitting Machine. U. S. Patent 1,134,747. W. B. KEIGHLEY, Vineland, N. J.

Machine for Pebbling Leather. U. S. Patent 1,137,119. J. R. CAMERON AND W. J. DENNIN, Elizabeth, N. J.

Drying Patent Leather. U. S. Patent 1,137,671. HEINRICH SHULZ, Worms, Germany. The leather is subjected to the action of light and of ammonia vapors.

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The American Leather Chemists Association

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Oma Carr, to % Champion Fiber Co., Room 1577, 50 Church St., New York City.

Paul M. Randall, to Lowell, Mass.

Robert P. Cushing, to % Cattaraugus Tanning Co., Olean, N. Y.

Otto Kress, to % Forest Products Laboratory, Madison, Wis.

NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES.

The exposition opens at the Grand Central Palace, New York, Sept. 20, 1915 and continues throughout the week. Many of the exhibits which have been arranged for will be working units, showing processes and apparatus in operation.

It is expected that President Wilson will be present and participate in the opening. Among the institutions which are co-

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operating in the exposition are the American Chemical Society, the American Electrochemical Society, the American Institute of Mining Engineers, the American Institute of Electrical Engineers, the American Pulp and Paper Association's Technical Section, and the Bureau of Commercial Economics.

The program of the Exposition is as follows:

MONDAY, SEPT. 20.—Opening Day.

TUESDAY, SEPT. 21.

D. P. Pierce (Barber Asphalt Co.), "Work with the Ultramicroscope."

Howard H. Gross, President of the Tariff Commission League, will lead a discussion on the tariff.

R. S. Frinck (Frinck Pyrometer Co.), "The Relation of Chemistry and Mechanical Manipulation to the Evolution of the Glass Industry."

Harrington Emerson (The Emerson Co.), "Efficiency."

WEDNESDAY, SEPT. 22.

Thos. H. Norton (U. S. Dept. of Commerce), "Foreign Markets for American Chemicals."

F. W. Keogh (Pres. Nat. Assoc. Manufacturers), "Accident Prevention in the Chemical Industries."

Welding Ring (Pres. American Exporters' Assoc.), "Transportation and Shipping Facilities with Foreign Countries."

I. F. Stone (Pres. Natl. Aniline & Chemical Co.), "The Aniline Dye Situation."

J. L. Lightner (Hershey Chocolate Co.), "The Manaufacture of Chocolate."

THURSDAY, SEPT. 23.

J. L. Taylor (U. S. Bureau of Mines), "Explosives."

H. A. Huston (German Kali Co.), "Potash."

Linn Bradley (The Research Corporation), "Solution of Smoke, Dust and Fume Nuisances by Electrical Precipitation."

Percy Wilson (Secy. Assoc. of American Portland Cement Manufacturers), "The History of Cement."

Meetings of the American Pulp and Paper Association, Technical Section.

FRIDAY, SEPT. 24.

S. P. Sadtler, "American Contributions to Industrial Chemistry."

W. D. Coolidge (General Electric Co.), "The X-Ray."

Joint meeting of New York Section of American Chemical Society and American Institute of Chemical Engineers.

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SATURDAY, SEPT. 25.

John Barrett (Director, Pan-American Union), "South American Opportunities."

G. Frank Lord (DuPont DeNemours Powder Co.), "Farming with Dynamite."

G. B. Heckel (New Jersey Zinc Co.), "Zinc."

A large number of moving pictures, illustrating chemical processes, etc., will be shown.

Members of the American Leather Chemists Association who intend to visit the Exposition should apply to the Secretary, H. C. Reed, 227 Fulton St., N. Y. for tickets.

FAT EXTRACTION OF LEATHER.

By L. E. Levi and A. C. Orthmann.

In a laboratory which handles a large number of analyses, after the greatest practicable accuracy and efficiency have been attained, the next question to consider is economy in all its phases. It does not necessarily impair the accuracy of a determination to introduce methods which reduce the cost of the apparatus employed. Where many different kinds of substances must be analyzed, a great variety of apparatus must be kept on hand. In order to offset the expense incurred in buying apparatus which spends most of its time on the shelves or in the stock room, but must be on hand for the occasional analysis which demands it, the glassware that is used in the daily routine work should be selected with care, for it is this item that that generally makes the debit side of the ledger look incredibly large. With this point in view the authors offer to the members of the Association their experience with a simple yet efficient method for the extraction of fat in leather, hoping that the publication of these results may be a step toward the goal of complete standardization and simplification of methods, and at the same time reduce the cost of glassware used. The Soxhlet fat extractor, now almost universally used by chemists, is a delicate piece of apparatus, and entails great expense on account of breakage. Not every city is so fortunate as to have skilled glass blowers who can be called upon to repair broken pieces, so a Soxhlet which is out of commission

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must either lie around to be further broken and rendered entirely useless, or packed up and shipped at once to some distant point, the packing and expressage costing more than an entirely new Soxhlet.

We have only considered the direct monetary side of the Soxhlet and a word about man's most precious element, time, would not be out of place. The simple method described below has advantages over the Soxhlet in the saving of time, in that there is no need of constant regulation of temperature, no leaky corks, and, chiefly, no constant attention and no other chemist awaiting the completion of your work in order to obtain the extraction apparatus for his use.

Having some 2,000 leather analyses to make annually, the two factors above mentioned, received our most serious attention in respect to the fat extraction of leather by the Soxhlet method. Shortly after adopting this method in our laboratory our attention was directed to a method published by E. Goldberg in *Ledertechnische-Rundschau,* 1912, 49-50 (see abstract, this J., 1913, p. 58), in which the author uses trichlorethylene as a solvent and shakes for one hour. We have not tried out this method, but do believe that trichlorethylene has too high a boiling point for the purpose of extracting fat from leather and the temperature of expelling the solvent from the extracted fat would undoubtedly injure some of the fats found, thereby obtaining inaccurate results.

Our method is as follows:

Place 10 grams of the finely divided leather into a 250 cc. bottle, add 200 cc. of petroleum ether, stopper the bottle well, and let digest 24 to 72 hours, according to the time allowed for reporting the result, during which time shake the bottle and contents frequently. Then withdraw 100 cc. and place into a tared dish or flask, evaporate the ether, dry and weigh in the usual manner, multiply the weight by 20 which gives the per cent. of fat.

As a rule we have 20 to 30 or more leathers to analyze at one time, in which case the first determination considered is the fat, while this is digesting other determinations such as are necessary are made and in some cases the fat extraction is allowed to digest

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more than 72 hours or until the other determinations are complete. The following are comparative analyses by the Soxhlet and the above method:

Leather number	Per cent. fat by Soxhlet method	Per cent. fat by cold digesting method	Leather number	Per cent. fat by Soxhlet method	Per cent. fat by cold digeting methods
1	1.53	1.31	17	9.77	9.38
2	1.53	1.56	18	9.37	9.39
3	2.24	2.12	19	10.84	10.42
4	3.38	3.24	20	11.87	11.85
5	4.12	3.75	21	12.93	12.72
6	4.32	4.00	22	13.29	12.95
7	4.00	4.02	23	23.30	23.29
8	4.09	4.03	24	25.25	25.32
9	5.71	5.35	25	25.58	25.95
10	5.73	5.54	26	26.38	26.63
11	6.42	5.91	27	28.02	27.58
12	6.25	6.19	28	28.31	27.81
13	6.67	6.81	29	30.49	30.15
14	7.65	7.24	30	30.65	30.53
15	7.76	7.70	31	32.40	32.30
16	8.87	8.60	32	35.92	35.53

The above analyses by the cold digestion method were allowed to stand about 48 hours. The leathers analyzed were mostly heavy side leathers which contained a large variety of different fats such as wool grease, paraffine wax, sulphonated cod and castor oils, neatsfoot oil, tallow, stearine, soap, cod oil, sperm oil, mineral oils, etc.

We also had occasion to make several duplicate analyses by the Soxhlet method on leathers containing high percentages of fat, using the same sample for each analysis, and found that the Soxhlet method showed varying results on the same sample of leather. Results showed a difference as high as 1 per cent. For this we cannot blame the method but the sample of the leather itself. The impregnation of leather with fats, greases, etc., is never uniform and therefore it is an impossibility to obtain a homogeneous sample.

After the publication of our article (this JOURNAL, July, 1914) we had hopes of seeing the methods used by our various members given to the association through our JOURNAL, but have been doomed to disappointment, undoubtedly due to the pressure of

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other work, but hope in the very near future to have the pleasure of reading articles upon the methods used in the laboratories of our associates.

Laboratories of Pfister & Vogel Leather Co.,
Milwaukee, Wis.

July, 1915.

MOELLONS AND HARD GREASES.

By Dr. Gebhardt Bumcke.

Against the proposed method for analysis of moellons I have some objections and offer the following changes for consideration:

Moisture.—The heating over an open flame leads to losses of oily matter especially when light mineral oils are present. The size of the dish, the varying heat of the flame with different operators, the distance of the flame from the dish are other items that cause variable results. Beside this, 3 grams is a very small quantity for a test of a material that is so little uniform as the moellons are. All these objections are overcome by applying Marcusson's method for determining the moisture by distilling 20-50 grams of the sample with 100 cc. xylol using a 500 cc. flask, adding a little pumice stone to avoid bumping and heating the flask in an oil bath. As the commercial xylol boils between 270°-290° F., all water is driven out and collected with the xylol in a tube graduated in 1/10 cc. for 25 cc. carrying a bulb of 100 cc. capacity at the upper end. If any volatile oily matter is present it is carried over with the xylol and remains dissolved in it. After standing for several hours or over night the xylol has cleared up and the drops of water adhering to the walls of the tube can be pushed down with a feather attached to a wire. The results seldom vary more than 0.5 per cent., the difference in most cases being only a few tenths of a percent. This method is applicable to all oils and greases, emulsions and even soaps when heated carefully as the latter show great tendency to foaming.

Ash.—For the ash test 8-10 grams material should be used. When the water is driven off and the oil hot enough, a piece of ashless filter paper may be used as a wick to burn the oil, removing the burner while the oil is burning.

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Unsaponifiable.—For a moellon with 10 per cent. or more unsaponifiable 4-5 grams material may be sufficient, while of a product containing less than 10 per cent., 10 grams should be used. (For these weighings accuracy in the second decimal is entirely sufficient while only the result should be weighed on the analytical balance.) For 5-10 grams moellon 4-8 grams KOH (sticks) should be used, 30 cc. alcohol added (95 per cent. is not necessary 80-90 per cent. alcohol, as that recovered from other tests is sufficient) boiled with reflux condenser for one hour, shaking occasionally. The use of glass beads or pumice stone is recommended to prevent bumping. After the boiling, not 50 but only 25 cc. of water should be added to make the alcoholic solution about 50 per cent., or half water, half alcohol, to avoid dissociation of soap by which fatty acids could get into the petrolic ether. Transfer into a separator, rinsing the flask several times with petrolic ether (B. P. not over 60° C.). For the first extraction not less than 75 cc. petrolic ether should be used; for the following 40-50 cc. are sufficient. In most cases 3 extractions with petrolic ether may be sufficient, but as some cases have been observed where 6 or 7 extractions were necssary, the last extraction should always be tested whether oil is still present by dropping a few drops of the petrolic ether on paper and the extraction only considered as sufficient when no oil spot or ring can be noticed on the paper after the petrolic ether is evaporated. For breaking emulsions a little 95 per cent. alcohol may be used, or better a little alcoholic KOH solution. The combined petrolic ether solutions should be washed with 10-15 cc. of 50 per cent. alcohol to which a little phenolphthalein is added. The washing should be continued until the alcoholic layer remains white. Three washings will be sufficient in most cases, but sometimes 4 or 5 may be required. The question of drying is a very uncertain one and no universal time or temperature can be given. In my opinion this is the greatest cause for discrepancies in the results. Known mixtures of the same base with three different mineral oils in which the known amount of mineral oil was determined by the Spitz & Hoenig method, treated under the same conditions, showed that for one mineral oil six hours drying at 95° C. was just sufficient while the second had still an excess over the quantity applied and the third had lost 1-2 per cent.

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If degras or woolfat is present the extraction with petrolic ether is not satisfactory as some of the higher alcohols remain dissolved in the alcoholic soap solution while on the other hand, the soaps of the woolfat are not entirely insoluble in pertolic ether. Unfortunately these two errors do not compensate each other. Sulphuric ether extracts more unsaponifiable out of the woolfat but the ether dissolves still more soap than the petrolic ether. The real amount according to Holde, can only be found by saponification with 2N-alcoholic KOH under pressure in a sealed tube, heating three hours at 105° C. (in a salt water bath) rinsing the contents with alcohol into a dish, evaporating the alcohol, dissolving in water, precipitating the soaps with $CaCl_2$ solution (using 10 per cent. excess over the amount calculated by saponification value) filtering the precipitate, washing on the filter with diluted alcohol (1 alcohol : 20 water) till wash water with a few drops of $AgNO_3$ solution becomes only a little opalescent, drying the precipitate in the air then at least 48 hours in a vacuum dessicator, and extracting in a Soxhlet the entirely dry precipitate with acetone, freshly distilled over calcium chloride. The acetone solution is then cooled off, filtered into a tared flask, the filter washed with acetone, the acetone distilled off and the flask with contents dried at 105° C. for one hour, cooled and weighed. The extract must be neutral and free of ash.

A separation of mineral oil and paraffine from the unsaponifiable of the woolfat can be made either with acetic acid anhydrous or a solution of methyl-ethyl-alcohol (1 : 1) in which the mineral oils and paraffine are only slightly soluble..

While this whole process is rather tedious and takes much time, we could use the Spitz & Hoenig method for the determination of the amount of wool grease if we knew that, for instance, out of the 48 per cent. unsaponifiable in woolfat, 35 per cent. are found in the petrolic ether extract; (these figures have to be determined by further analytical data.) Unfortunately the amount of unsaponifiable in pure woolfat varies from 43-52 per cent. so that, even if we knew that we retain about 73 per cent. of the woolfat-unsaponifiable in the petrolic ether we could only come to approximate results when determining the amount of woolfat present. In case the presence of woolfat is found by the Lieber-

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mann[1] or Hager-Salkowski[2] tests the unsaponifiable should be tested for mineral oil or paraffin wax:

First: By determining the iodine value which for the unsaponifiable of woolfat is about 30 or higher.

Second: By solubility in anhydrous acetic acid.

Third: By solubility in methyl-ethyl alcohol (1 : 1).

By the two latter methods the mineral oil products can be separated and their character can be determined. (Mineral oils have iodine values about 6-15, except some from "crack" distillates which are much higher, while the iodine value of paraffine wax is below 1.)

Oxidized Fatty Acids.—It is not necessary that the soap solution of the unsaponifiable determination be used, but 4-5 grams of the sample may be saponified as above, after saponification the alcohol expelled, the soap dissolved in hot water, rinsed in a separator and an excess of HCl added. This gives about 150 to 175 cc. When cool at least 100 cc. petrol ether are added and the funnel vigorously shaken. A persistent emulsion is broken by the addition of a little HCl. After standing for a couple hours the aqueous layer is drawn off through a filter to catch oxidized fatty acids suspended in the water, the petrolic ether washed twice with water or in cases of difficult separation with diluted HCl (1 : 10), the wash water run through the same filter. The filter is washed with water and dried in a warm place (not in the oven). Through the dry filter the petrolic ether is run into another flask and the larger part of the oxidized fatty acids, which is left in the funnel, washed twice with petrolic ether, which is run off again through the same filter. The latter is washed with petrolic ether. By running the aqeuous as well as the petrolic ether solution through a filter, usually no losses of oxidized fatty acids occur. The oxidized fatty acids in the funnel are then dissolved in hot alcohol and run through the same filter

[1] One-half gram of the sample or better ¼ gram of the unsaponifiable is shaken with 3 cc. Acetic acid anhydrous in a test tube for 1 minute, the acid filtered off through a small filter and one drop concentrated H_2SO_4 added, a pink to brown color that turns soon into a lasting green indicates the presence of woolfat.

[2] One-quarter gram of the unsaponifiable dissolved in 10 cc. chloroform, shaken with 10 cc. concentrated H_2SO_4 shows a blood red color with strong green fluorescense of the acid when woolfat is present.

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into a tared flask, the filter washed and the alcohol distilled, the flask dried over night or at least for six hours at 95° C. (in a steam oven) cooled and weighed. The whole operation should be done with as little delay as possible as the fatty acids of the moellon are liable to oxidation when exposed to the air too long, even in the form of soap. For this reason it would also not be right to redissolve the dried oxidized fatty acids in alcohol, filter them and evaporate the alcohol, cool and weigh again. Every time this procedure is repeated a loss will occur as some of the oxidized fatty acids are further oxidized so that they become insoluble in alcohol. I have found dubbing greases and moellons that had a rather high amount of such oxidized fatty acids (probably polymerized) which were insoluble in alcohol and even only slightly soluble in benzol.

The amount of water-soluble oxidized fatty acids seems a negligible quantity and if we try to recover them we probably do not find the true quantity as the other water-soluble fatty acids may be partly oxidized during the process of recovery.

Free Fatty Acids.—For the determination of free fatty acids it seems not advisable to use such a small quantity as 1 gram moellon in 40 cc. alcohol-ether (1 : 1). The change from acid to alkali with phenolphthalein cannot be observed very plainly with most moellons on account of the dark color. I would recommend 8-10 grams moellon in 50 cc. alcohol (or alcohol-ether) and as indicator 1 cc. of a 1 per cent. solution of "alkali blau 6 B" from Meister, Lucius & Bruening which is also recommended for all dark greases. This indicator is blue with acid and red with alkali and the change can be noticed much more clearly than the slight change from colorless to pink of phenolphthalein in a brown solution. Though it is not quite so sensitive as phenolphthalein, the error made is negligible compared to that which may occur while titrating moellons and dark greases using phenolphthalein as indicator.

Mineral Acids.—Mineral acids are seldom present and if so only in small quantities. To determine their presence qualitatively and quantitatively 100 grams of moellon in a 500 cc. Erlenmeyer are heated with 100 cc. distilled water on the water bath, shaking frequently. Some drops of methylorange are added.

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If acid is present the hot mixture is transferred into a separator, the water drawn off and titrated, poured back into the separator, the water with the moellon shaken well and after settling the water again drawn off and titrated. This is repeated till the water remains yellow. This test is applicable to all oils and greases (except sulphonated oils).

Soap.—The presence of soap is determined qualitatively by shaking the moellon with an equal amount of hot water (as above) but adding phenolphthalein to the water. As all soaps are dissociated by hot water, a pink color will indicate their presence.

For a quantitative test for soap 10 grams should be weighed into a separator containing 50 cc. water, 100 cc. sulphuric ether added and 25 to 50 cc. normal HCl according to amount of soap present. Another shaking with 20 cc. water plus 10 cc. N/1-HCl should follow. The ether layer is then washed with water till free from mineral acid and the combined quantities of water and acid titrated with N/2-NaOH. From the result the amount of alkali present is calculated and the amount of soap with fair accuracy found, by taking 312 as mean value of the molecular weight of the fatty acids, if it is not required to determine the molecular weight for greater accuracy.

Hard Greases.

My objections to the proposed methods and my counter proposals are contained in the following:

Melting Point.—Method A should not be accepted as no two capillary tubes are alike in width and thickness of glass. More or less air in the capillary tube will help to drive up the grease with more or less force; if the tube is sealed, the expansion of the air in the sealed end will also have some effect. This method will only give exact results in different hands if the same amount of grease is heated under exactly the same conditions. The difference is obvious so long as everybody makes his own capillary tubes. Another objection is that some greases do not become clear, thereby causing differences.

Method B is rather crude though the suggestion of Mr. Small to immerse the test tube in water makes it considerably better. Here too exact dimensions should be given for the size of the

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test tube (3 cm. wide, 22 cm. long) the distance of the thermometer bulb from the bottom of the test tube (2 cm.) the size and shape of the bulb of the thermometer, also the time for rise of 1° in temperature. All these items could be standardized, except (and this is the main objection against this method) the amount of grease adhering to the thermometer bulb. The hotter the grease the less will adhere to the bulb, the nearer the temperature is to its melting point, the more will adhere to it. But even when in all cases the temperature of the grease is just 5° C. above its melting point, it will only be with great difficulty that the same observer can get the same amount of grease on the bulb of the thermometer. Only when the same amount of grease adheres to the bulb are the conditions for the first falling drop nearly the same. The amount of grease will always be an uncertainty with different observers and for the reason this method should not be accepted.

The same observations and conclusions led Ubbelohde to design his apparatus for the melting point of fats and greases, or as he calls it more correctly the "drop point," as every grease is melted before the first drop drops down. All the items of Method B even the amount of grease, are standardized in Ubbelohde's method. While with Method B, I often had to be contented with a difference of 1-5° C., I seldom experienced a greater difference than 0.2° C. when using Ubbelohde's method. I strongly recommend this method for adoption as the official method for all greases, fats and waxes.

For the melting point (drop point) of paraffine wax the Ubbelohde method should also be accepted as it fits for this just as well as for any other wax or grease. The method prepared by the committee, the so-called "English method," (which by the way was given by Finkener some 20 years ago only with standardized conditions and a small, inexpensive apparatus designed by him) does not give the melting point, but the solidifying point of the paraffine wax. It is no wonder then that in the report of the committee published in December 1914, page 557, the conclusion was made that the Ubbelohde method did not agree with the Saybolt or English method. Those gentlemen have entirely overlooked that the solidifying point as given by two methods

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must differ from the melting point which is given by the Ubbelohde method.

For determination of the solidifying point I would recommend the method by Shukoff which is more precise giving only differences of a few tenths of 1° C. Exact dimensions of the vessels are given and a description of this method is found in *Chem. Ztg.*, 1901, 25, No. 95 or in Holde, *Untersuchung der Mineraloele & Fette*, 1905, page 251.

Unsaponifiable.—For the determination of the unsaponifiable I recommend the same conditions and operations as outlined for Moellons.

Free Fatty Acids.—I object strongly to the use of such a small quantity as 1 gram. Even if the sample is all fatty acids I take 1-2 grams weighed on the analytical balance. 5-10 grams should be used according to free fatty acids present. I call attention to the remarks of Fahrion about the acid value. pp. 8-10, 1915 January number of this JOURNAL, especially the last paragraph.

When 10.00 grams grease or oil are used, a lye containing 19.90 grams KOH in one liter will indicate per cent. of oleic acid by direct reading, 1 cc. representing 0.1 gram oleic acid or 1 per cent. of 10 grams grease or oil. Where many tests have to be made daily, much time is saved by not weighing but measuring the oil or melted grease in a small funnel tube with stopcock and a globe containing 10.9 cc. = 10 grams oil or melted grease from cock to upper mark. After running the oil from the funnel into a 250 cc. flask, the funnel is rinsed with neutralized alcohol-ether (1:2) after addition of a little phenolphthalein solution and titrated till the alcohol-ether after sufficient shaking remains pink, the number of cubic centimeters used gives directly the per cent. of free fatty acids present in the grease or oil. For very dark grease the use of "alkali blau 6 B" (Meister, Lucius & Bruening) is recommended as for moellons.

I cannot understand why (as Mr. Eachus states) greases with melting point above 120° F. should not be fully saponified in alcohol solution with excess of alkali boiling for one hour. I found that they usually are entirely saponified after fifteen minutes. The only difficulty arises when waxes, to which degras (woolfat) belongs, or much unsaponifiable is present, because the

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waxes, as in well known, are harder to saponify and great quantities of saponifiable are liable to include some of the saponifiable and protect it against the influence of the lye.

As the unsaponifiable of waxes is soluble in hot alcohol no petrolic ether is necessary and one hour boiling over a flame with the necesary excess of alkali is sufficient for complete saponification. Petrolic ether should only be added if mineral oil or paraffine wax are present in large quantities.

Laboratory of F. S. Walton Co.

THE SPECIFIC GRAVITY OF LEATHER AND ITS COMMERCIAL APPLICATION.

By Oskar Riethof.

As most of the European chemists, when I first came to America I stated on my leather analysis reports the specific gravity of the sample. This led to discussion with different American chemists about the value of the specific gravity figure of leather, and I have been asked by a number about the method I employ in taking the specific gravity and about the practical use I claim for it. In attempting to write on this subject I make no pretentions of bringing anything new, but am only restating the method employed in Europe for many years.

As every chemist and practical tanner takes and uses the specific gravity figure on tan liquors, extracts and oils, it would not seem necessary to define "specific gravity," but for the sake of completeness a short definition may not be amiss:.

The specific gravity is the relation between the weight and the volume of a substance. For solid and liquid substances, the specific gravity of water at 4° C. is the unit. The specific gravity therefore shows how many times a solid or liquid substance is lighter or heavier than the same volume of water at 4° C. The weight of the unit volume—1 cc. of water at 4° C.—is 1 gram. The specific gravity of any substance is therefore equal to the weight of the unit volume. Let W equal the weight of the substance in grams, V the volume and S the specific gravity, then

$$W = VS \text{ or } S = \frac{W}{V}.$$

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The barkometer indicates the excess weight in grams of one liter of the liquid over one liter of water.

As explained, the specific gravity of leather shows us the relation between volume and weight, or if we speak in terms of the sole cutter—the cutting result. If the cutter buys two kinds of leather at the same price, he will cut soles cheaper, other conditions being the same, from the product having the lower specific gravity. The same holds good for belting leather. In fact, I know many cases in Europe where sole, belting leather and belting, when handled by the pound, are sold on specific gravity basis (generally 1.0), so that the buyer gets a discount if the leather falls heavier than contracted for. The specific gravity, therefore, gives us a simple way to compare the cutting value of different leathers.

It is readily understood that the specific gravity of leather depends upon plumpness and load. In making specific gravity determinations regularly, the tanner is able to note any marked change in this figure. Suppose there is an increase. By comparing his specific gravity with the gain, he is able to determine whether the higher specific gravity is due to lack of plumpness or to greater loading. The aim of the tanner must be to get a product with the highest possible gain at the lowest possible specific gravity: in other words, high gain combined with plumpness. It is readily comprehended that to work to this end the specific gravity figure is of great aid.

All that is needed for the determination is a metric system ruler and an instrument, graduated to tenths of a millimeter, for measuring the thickness of the sample. A very accurate device of this kind is made by Arthur Meissner, Freiberg, Sa. (Germany).

For the determination, cut a piece of leather from 8 to 10 centimeters square, taking pains to cut the edges perpendicular to the surface. Divide the surface, checkerboard style, into squares measuring 1 to 1½ centimeters on a side; the smaller the divisions, the more accurate will be the determination. Then take the average length of the sample by measuring the different sections and calculating the average. Take the average width in the same way. Then with the aid of the instrument mentioned

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above, estimate the average thickness by noting down the thickness of each section and calculating the average. Then the length, times the width, times the thickness gives us the volume. We have just to divide the weight by the volume to get the specific gravity.

Of great importance, and only too often neglected, is the part of the hide, from which the sample is taken; for the different parts show different specific gravities. The results obtained from some American and foreign sole leathers will illustrate this. The figures in the horizontal rows give the results of three samples taken from the same side, one each from the back, shoulder and belly respectively.

Back	Shoulder	Belly
1.11	1.08	1.68
1.06	1.04	1.02
1.07	1.03	1.02
1.15	1.13	1.08
1.11	1.08	1.04
1.00	—	0.99
1.03	—	0.97
1.03	—	1.00
1.07	—	1.00

As a rule the back shows the highest specific gravity, approximately 5 per cent. higher than the belly, the shoulder falling between the two. For comparing results it is best to take the sample from the back.

To show the great differences in specific gravity of the same kind of leather I will quote following, the lowest and highest values obtained during the experience of the writer:

Vegetable tanned shoe leather	0.90 to 1.20
Vegetable tanned belting and harness leather	0.90 to 1.30
Chrome sole and belting leather	0.70 to 1.00
Chrome tire leather	0.65 to 0.85

Richwood, W. Va.
August, 1915.

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IGNITION OF MAGNESIUM PYROPHOSPHATE.*

By S. H. Champlin.

In making determinations of phosphorus or magnesium, it has been found difficult to ignite the magnesium pyrophosphate to complete whiteness, even with greatest care, when the usual methods are followed. The operation may be carried out quickly and easily as follows: Place the wet filter and precipitate in a Vitreosil crucible and dry over a low flame, inclining the crucible on the triangle, and resting a cover against the top so as to cause the warm gases to circulate over the paper. When the paper begins to brown, place the crucible, uncovered, in a muffle below a red heat and smoke off the paper. Cool, and saturate with nitric acid (sp. gr. 1.42). Warm gently to expel the excess of acid increasing the heat slightly until red fumes come off. Return to the muffle, now at a dull red heat, and ignite until the evolution of red fumes ceases. Then raise the temperature to a bright red heat and ignite until constant weight is obtained.

The use of a platinum crucible has never been attempted on account of the danger of alloying.

Camden, N. J.

NOTE ON THE IGNITION OF MAGNESIUM PYROPHOSPHATE.

By L. A. Cuthbert.

In the preceding article from the *Chemist-Analyst,* No. 14, Mr. S. H. Champlin describes a rapid method for the ignition of magnesium pyrophosphate precipitates. It is well known that precipitates of such character can be burned to constant weight much more quickly provided the precipitate is dried and the paper charred without burning before igniting the precipitate to a red heat. For charring any paper without burning it, a simple and convenient method which requires no attention at all, and the material for which is found in all laboratories, is as follows:

Invert a common 2-in. poreclain crucible top such as comes with the ordinary porcelain crucible and place in a larger size

* *Chemist-Analyst*, No. 14, p. 8.

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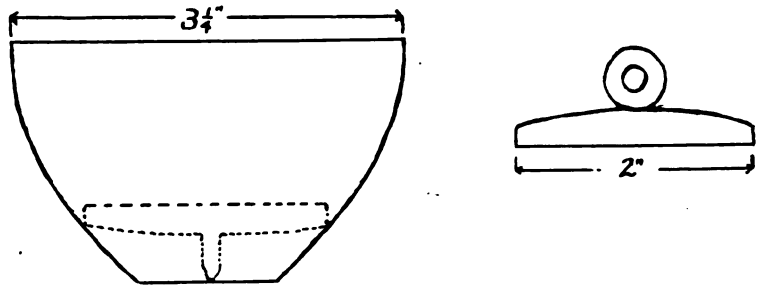
porcelain crucible, preferably a crucible with a 3¼ in. top, 1⅛ in. bottom and 2 in. height, as the ordinary 2 in. top will rest snugly in this size and will not tip over very easily. Place the wet precipitate and filter paper in a platinum crucible and set the crucible



on the inverted porcelain top. Heat slowly at first to drive off the moisture and when dry heat over the hottest flame of the Meeker burner or blast lamp until the paper is thoroughly charred. No attention is required as the paper does not burn. When charred, remove the platinum crucible and burn in the usual manner to constant weight.

Elk Tanning Company Laboratory.

DRUM TANNING.*

By Professor Dr. Edward Nihoul.

Drum tanning has for many years been rapidly supplanting, on the continent, the older method of tanning in the pits. This method of tanning shows advantage not only from the point of view of cost, but also from the point of view of quality of the finished product. The object of the author in writing this article is not with a view to describing the method of working in its latest details as full particulars of these can be obtained from manufacturers selling tanning extracts, apparatus manufacturers, and other specialists whose business is to complete installations for drum tanning purposes; the writer will therefore content himself with answering the two following questions:

* *Leather Trades'* Year Book, pp. 180–5, 1915.

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1. What is the object of drum tanning, and what are its advantages?
2. Does the method depend upon scientific factors, and is it possible by this means to produce a product which will compare favorably with those obtained by the older fashioned systems of tanning?

1. *Advantages of Drum Tanning.*—Formerly people said when speaking of the tanners' profession that this was principally dependent upon two chief factors, (*a*) tan, (*b*) time. The importance of the first-mentioned is diminishing more and more, owing to the improvements of the mineral tanning on the one side and to the introduction of concentrated extracts and synthetic tannins on the other. In respect of the second factor it may be said that this is now reduced to a minimum, whilst future methods will perhaps effect a still further diminution of the time of tanning. In connection with this matter the author would state that some Belgian tanners buy their hides at the big markets of Antwerp and Hamburg on a six months' bill and actually sell the leather manufactured by drum tanning on three months' terms, thereby receiving payment for the finished product before payment for the raw material becomes due.

In the manufacture of sole leather, by drum tanning, the ideas inculcated in the old industry disappear, namely: (1) accumulations of large quantities of goods in the pits; (2) the considerable difference which often occurs between the price of raw materials, and especially hides, at the time of commencing the work, and the price of these same materials at the time when the manufactured product is ready for sale; (3) the liability of the deterioration of the quality of the product by formerly little known factors, sometimes of unknown origin, such as bacteria, etc., which have their action in the liquors which were kept for long periods of time. It was formerly necessary for the tanner to employ a considerable amount of capital, and to apply his activities to the commercial side rather than the manufacturing, or to become entirely dependent upon the good-will of the leather merchant to advance to him the necessary money to enable him to carry on his business.

In the *Leather Trades' Year Book,* 1914, Professor Procter

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summarizes the great progress which has been made in the chemistry of leather manufacture during the past 40 years. The technical developments of the leather industry form a sequel to the work of the scientists, and drum tanning is one of the many results of laboratory work.

2. *Discussion of the Method.*—The primary factor in tanning depends on the combination of the tannin with the hide substance. Let us consider the chemical side of the tanning question for the moment. It has been known for some considerable time that the state of a substance which is most adaptable to chemical reaction is the liquid state. In order that the reaction may take place it is necessary that the molecules should come into contact with each other. In the gaseous state the molecules are apart from each other and consequently the reaction is slow. In the solid state the molecules are not mobile enough to enable the reaction to be sufficiently quick to become industrially applicable. The complexity of the molecules has a very important bearing on the speed of the reaction; the more complex the molecule, the slower is the reaction. It should be duly noted, however, that the reaction though slow is possible and that the reaction may take place in some chemical industries sufficiently quickly under these conditions, provided the *vis-viva* of the molecular movements is sufficiently increased by the application of heat.

With a view to increasing the rate of the reaction in the case of solid substances, several methods are employed for the purpose of bringing the substances to as near as possible, the liquid condition. The reactions between gases are quickened by the use of pressure, or by substances called catalysts (for instance, in the manufacture of sulphuric acid by the contact process), in order to increase the density, to condense them, and to bring together their molecules. In the case of solids the reverse methods are employed, either the *vis-viva* of the molecular movements is increased by supplying them with sufficient additions of heat. This is the method adopted in the manufacture of ceramic products where reactions take place between solids. When it is practicable, solids are liquified by the use of heat, as in the manufacture of glass, when the reaction takes place in the molten condition; or again, the reaction is effected by the use of an inter-

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mediary solvent, liquifying the products, which can then react. This latter is the method adopted in the manufacture of a large number of chemical products.

The primary condition of every chemical reaction is to obtain as close contact as possible between two compounds, hence the necessity for the mechanical preparation of the solids which are required to react is important. In order that two solids may react with each other it is necessary that they should possess sufficient chemical affinity.

Having discussed the rudimentary outline of chemical reading, let us now see what happens in our own industry. First of all, do the two bodies (namely, hide substance and tannin) possess sufficient activity to enable them to react? In order to have an affirmative answer to this question it is sufficient to pour a solution of tannin into a solution of gelatine. The reaction is complete and instantaneous. Unfortunately, though it is possible to give to the molecules of tannin the required mobility by dissolving in water, it is not the same with the hide, as the object of tanning is principally to make the fibers of the hide water resisting, and to allow them to slip over each other with more or less ease, according to the kind of leather one wants to manufacture. It is, therefore, impossible to dissolve the hide, and in consequence a particularly disadvantageous position arises, viewed from the standpoint of the rapidity of the reaction; the close contact between the tannin and the fibers of the hide is extremely difficult to effect. Some attempts, however, have been made in this direction.

It is possible to obtain a more direct contact by sucking the solution of tannin through the hide by means of vacuum, but though the attempt has been made in Belgium it has not yet been found to be industrially successfully owing to the cost of the necessary installations. In spite of the good qualities of the leather produced in this manner, same only derives a very small gain in weight. The complete tanning of a skin might be done by this method in some days, with a solution containing as little as 1 per cent. of tannin. The leather so manufactured has superior qualities for mechanical purposes.

On the other hand, the rapidity of the penetration of the tannin

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through the hide is hindered by another factor, namely the tanning solutions themselves are diffused through with extreme slowness. Tanning materials have considerable molecular weights and are therefore put into the class of colloids, hence the necessity for protracted treatment by the latter process of tanning.

Another very important point is the fact that tanning liquors which impregnate the fibers, detannize quickly when in contact with these, owing to their dilution, but the penetration, owing to the immobility of the materials in the pits, is retarded by the more or less thick portion of non-tanning matter, becoming more and more concentrated and through which fresh tanning liquors penetrate exceedingly slowly. Tanning solutions on standing become turbid and give rise to the production of insoluble compounds which not only do not penetrate the fiber, but also settle on the surface, thereby retarding the penetration of the tannin left in the solution. In drum tanning these inconveniences are for the most part not encountered.

(1) Owing to the fact that the goods in the liquor are being moved continuously, thereby bringing the surface of the goods in continuous contact with the tanning liquor, and the revolving of the drum has the effect of folding and unfolding, with the result that when pressure is applied by the folding, the tannin in the skin is pressed out and replaced with a further quantity of liquor containing tannin, thereby considerably hastening the penetration of the tannin in the hide.

(2) The easily oxidizable and fermentable tanning materials are by this method penetrated through the skins before they become insoluble, and are enabled to react directly with the fibers of the skin; hence the whole of the available tannin is used and considerable saving thus effected.

(3) The constant tumbling prevents the liability of the permanence of super-saturated solutions. When like solutions penetrate through the skin it allows the substance in solution to precipitate, thereby increasing the yield. The semi-solid solution, owing to the movement of the tumbler, cannot settle on the hide and thereby hinder the tanning process. Light leathers are in this way more supple and of better quality. Sole leathers, requir-

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ing firmness and solidity, may be retanned in vats with filling substances in order to obtain the required result.

(4) The constant rubbing of the goods against each other and against the side of the drum conduces to the production of a slight rise in temperature; this without being expensive, facilitates the tanning by helping the phenomenon itself and by diminishing the viscosity of the solution. In large installations the drums are usually arranged in a series and are fitted with hollow axles which allow of the introduction of the strengthening liquors without stoppage of the vessel. It is desirable in the case of drums of large diameter to have the vessel suspended over a rectangular pit, with a view to diminishing the labor necessitated in loading and unloading, which occurs when the drum is fixed on to the floor, in which case the door of the vessel is usually somewhat out of the reach of the operator.

The working of the process is varied in different works. In some cases the liquors are of progressive strengths in the various vessels, and the goods are moved from vessel to vessel; in others the goods remain in the same vessel throughout the process. Drum tanned leather may possess a great gain in weight, but in this case, of course, the leather generally contains a large quantity of water soluble matter. When the operation is not properly carried out there is the liability of the goods being brittle.

The addition of various materials as adjuncts to the tanning liquors has been recommended from time to time; these taking the form of catalysts. These substances in some cases do not possess any action whatever, whereas in others they are actually detrimental, whilst in others they are efficacious either from the standpoint of protectors of the grain surface, or in the yield of leather. The increased yield brought about by the addition of such materials as these is particularly interesting, because it is extremely likely that the yield possesses definite relationship to the condition of the tanning materials.

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SYNTANS AND THEIR PRODUCTION.*

By E. Ethelbert Wilkinson.

Since the outbreak of the European war, chemists and manufacturers have given an increased amount of attention to the problem of producing synthetic tanning agents. The cessation of the supply of Neradol D is, of course, the main factor which has caused this increased interest in the subject; indeed, it has been a matter of surprise to find how widely Neradol has been used in this country.

The various products—of various manufacturers—which the writer has seen have varied in color from red-brown to black, and in consistency from a thin fluid as mobile as water to a stiff paste; and almost all of them have contained an appreciable quantity of insoluble matter.

From his own experiments in this direction, the writer has obtained a considerable number of products, and has carried out pelt tests with all the samples. Many of these "syntans" have been made according to the patent specification of Neradol D, with at most, very slight variations. The results of the first experiments were certainly fearsome-looking products, but these were improved upon until a substance was produced, sufficiently like Neradol D, to justify proceeding to try wider modifications of the original methods.

The substances required, according to the specification, are crude cresylic acid, sulphuric acid, formaldehyde, and caustic soda; and three distinct processes are involved—sulphonation, condensation and neutralization. Each of the substances used should be tested. In the case of the sulphuric acid, formaldehyde, and caustic soda, this is a simple matter. The cresylic acid offers more difficulty, but tests can be devised—one is mentioned later—which will give a sufficient indication of its suitability or otherwise, for the production of syntan. Crude cresylic acid consists of three isomeric cresols, with probably other phenols, and generally also contains a quantity of pyridine; this latter, however—present during the process as sulphate—does not interfere with any of the operations, and even its unpleasant smell is absent unless the substance is made alkaline.

* *Leather Trades'* Year Book, pp. 147–50, 1915.

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Sulphonation.—This consists in heating together equal weights of cresylic and sulphuric acids. Although this appears very simple, there is good reason to suspect that the faults of the majority of the English "syntans" have their origin in this process. Sulphonation should be complete, but not unduly prolonged. No definite time can be stated, as in different experiments the time necessary for complete sulphonation has varied between 1½ and 8 hours. The substance can be tested from time to time, but after a little experience, one can gauge fairly accurately the completion of the process, simply from appearance.

It may be pointed out that this sulphonated product can be utilized for roughly estimating the value of the cresylic acid. This is done by forming the barium salt of a weighed quantity of the sulphonated product, then precipitating the barium as sulphate by the addition of sulphuric acid, and weighing the precipitate. From this weight can be calculated the amount of cresol, with which the barium has been combined, and hence the percentage in the original crude cresylic acid. Of course, other phenols, which may be present, will be estimated as cresol, but as these will probably form tans similar to that which cresol produces, the error involved will not be great, and the test will be at least comparative.

Condensation.—From this point onwards, the rule is, "keep cool"; which rule may be applied both to the substance under observation, and also to the person controlling the operation; for the process now becomes very slow and tedious; and, although the formaldehyde vapors evolved are a decided change from the phenolic smells produced by the previous operation, yet it is doubtful if the change can be appreciated as an improvement.

The product of sulphonation is cooled, and a solution of formaldehyde is slowly run in, the mixture being continuously stirred, and kept below 35° C. The addition of the formaldehyde solution tends to raise the temperature considerably, both from the heat generated by the chemical reaction, and also by the mixing of the concentrated sulphuric acid, with the aqueous solution; so that even when the substance is cooled by means of ice or cold water, the addition can be conducted but slowly.

The substance, on the completion of this process, should be a

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dark-brown, very viscid liquid, with only a suspicion of redness. The product is hygroscopic, hence it should not be left exposed for any considerable time, before proceeding with the neutralization.

Neutralization.—The acidity of the substance at the end of the previous operation generally lies about 25 per cent., calculated as sulphuric acid. The third process consists in partially neutralizing this acidity. It is necessary to calculate the quantity of caustic soda solution required to do this for each separate batch. This is most easily accomplished by calculating the alkalinity of the caustic soda solution as due to H_2SO_4, *i. e.*, in the calculation, multiply by 0.049 instead of 0.040. The proportions then required are found by the following formula:

Acid solution—a per cent.
Alkaline solution—b per cent.
(Both calculated as H_2SO_4.)
To mix so as to leave x per cent. acidity.
Take: Acid solution $(b + x)$ grams.
Alkaline solution $(a - x)$ grams.

The acidity desirable is about equal to that of a normal acid solution, or 4.9 per cent. H_2SO_4.

Experiments lead one to suspect that this last operation, by a slight alteration of conditions, will entail much more than a mere neutralization, and may introduce more complicated chemical changes than either of the other two processes. If the solutions are mixed quickly, sufficient heat is generated to cause the liquids to boil. The specification gives 35° C. as the maximum temperature to which the substance may be allowed to rise. This again necessitates external cooling, and slow addition of the alkali. During the process, the substance becomes gradually more liquid, and lighter in color.

Although a good "syntan" can be produced by means of the chemicals and processes described, it is at least doubtful, if Neradol D is produced by strictly adhering to these details. The point in which the products differ from that of the Badische Co. is in the penetration, which is rather slower with the former, although otherwise the leathers produced from them are very similar. By varying either the manipulation or the constituents,

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or both, a vast field of possibilities is opened, and some surprising results have been obtained. Of the writer's experiments, as previously stated, some have been made with strict adherence to the methods stated, whilst some have varied more or less widely, both as regards the chemicals employed, and also the manipulation. Amongst the products of the latter class, a "syntan" has been produced which may be particularly mentioned. It is quite unlike Neradol D in appearance, and produces a pure white leather, very soft, yet tough, and what is perhaps more important, the total time which the pelt (calf) was in the tanning liquor, was only 5 hours.

THE CHEMIST IN THE SHOE FACTORY.*

By J. A. S. Morrison, M.Sc.

The advent of the chemist into the shoe factory is of such a recent date that it will perhaps interest leather men to be told of the experience of a leather trades chemist holding a position with one of the largest firms of shoe manufacturers in the country. In a short article suitable for this *Year Book* it would be unwise to go into too much detail. One or two phases of one's work may be of special interest, and in discussing them it is hoped that tanners will benefit thereby.

Of the main duties of a chemist the following may be mentioned:

1. The examination of all leathers—bottom stuff and upper.
2. The examination and production of various finishes.
3. The examination of faulty goods.

1. Broadly speaking, it may be said that very few upper leathers offered to makers of fine shoes are adulterated or are faulty. A few of the two-bath chrome tannages show smaller amounts of chrome than one would desire, and one would express the opinion that it seems to be a very short-sighted policy to cut down the tanning material when the cost under this head is only a small percentage of the cost of production.

Shoes made from under-tanned leathers generally burst in the vamp; and whilst decomposition is generally due to excessive

* *Leather Trades'* Year Book, pp. 143–6, 1915.

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perspiration it is my experience that, of two leathers, the one containing the most chrome will stand up better under these trying conditions. Again, some manufacturers degrease their glazed kid before finishing, and shoe makers find that such leathers give the finer looking shoe when finished. The usual shellac finishes do not take kindly to a greasy leather, and one experiences great difficulty in turning out the shoe so that it will immediately catch the buyer's eye.

Regarding bottom stuff; the writer's experience is that a very large number of tannages are so adulterated that the goods are of no use to the maker of fine shoes. Many firms of repute turn out bends, bellies and shoulders which contain small amounts of adulterants—say up to 2 per cent. of Epsom salts and 2 per cent. of glucose. Now these can only be due to the use of finishing extracts. Many tanners do not use them, and it is found that the pure tannages give the best results when the shoes are in the finishing room. I am passing over the fact that, as adulterated leathers, they do not give the best wear, and that in buying them shoe makers do not get value for their money, for the tannages finished with these extracts often cost as much as those which can be passed by the chemist as containing no adulterants whatever. I am afraid that many tanners use these extracts in order to save trouble in supervision of works processes.

Of late years there has been an increasing amount of unstuffed chrome sole. This material was originally used for tennis and deck shoes, but much of it is now put into children's shoes. I find very few tannages which do not contain considerable amounts of glucose. Two very well-known bends contain 9 and 13 per cent. respectively. One maker states most emphatically that it is not possible to turn out this class of goods without using glucose, whilst others offer chrome bends free from glucose at a higher price. There is no doubt that it is much more easy to dry out and finish chrome bends when they contain glucose, and the writer believes that this is the sole reason for its use. I am also firmly convinced that a lightly fat-liquored bend can be produced which will wear and look as well as the usual bend. Shoe manufacturers are continually receiving complaints that children wearing this class of shoe seldom have dry feet, and from a hygenic

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point of view this chrome sole is to be condemned. It is also noted that some brands of waterproof chrome sole do not give the water resistance which one would expect, and it will probably be found that these bends are impregnated with glucose before drying out in readiness for the stuffing process. There is a good opening for the chrome tanner who will steer clear of glucose when tanning this class of goods.

2. The question of shoe finishes does not concern the tanner to any great extent, but, in passing, it may be said that, from the point of view of the shoemaker, the leather with a minimum of finish will generally work best in the shoemaker's hands. Many upper leathers are so overloaded with finish that it cracks away in making up, and thus causes much trouble in the treeing room.

3. In considering faults which develop whilst finishing fine shoes two troubles immediately occur to me. Many soles are finished with quick black, and is found that a sole containing Epsom salts will not easily take a good finish. When one considers that these quick blacks contain large amounts of soap it is readily understood that magnesium soaps may be formed if Epsom salts be present in the sole. The formation of these magnesium soaps breaks the emulsion and we get curdling of the finish. The result is that the finish does not then give the required silkiness under the polishing wheel and we get breaking up of the surface. Having found that a particular tannage behaves in this way, the shoe manufacturer generally tries to use no more of it on future occasions.

Another serious difficulty which is experienced in fine shoes is "checking" of heels. My first "case" in a shoe works was a large rack of shoes in which the lifts of the heels were slowly parting company. A good shoe showing this fault is immediately to be condensed. Leather trades chemists know that the addition of magnesium sulphate to a glue considerably diminishes its powers of agglutination and we get a reproduction of this effect when we attempt to build a heel with lifts containing Epsom salts. Thus again, adulterated leather is not cheap to the shoemaker who caters for the high class trade.

In this short article I have tried to help tanners to a better understanding of a very few of the problems which continually

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confront shoemakers, and it is my hope that those tanners who take a real pride in their work will be encouraged thereby to make changes, if necessary, so that their products may be more suitable for use in the better class shoe trade.

ENZYMES.*

By J. T. Wood.

During the last few years tanners have occasionally come across the word "Enzyme" in the trade literature, and have, perhaps, not known what was meant by the term. I think there is no doubt in many cases they have been deterred from studying certain problems by the fact that the terminology employed was not understood. Unfortunately, one cannot study any branch of science without encountering words not in common use, but which are descriptive of certain actions or certain compounds, and are used by scientific men as a kind of shorthand. Sometimes the word contains wrapped up in it a whole world of meaning and explanation, as in the case of the names of the complex compounds from which aniline colors are made. Such a word as "diazoamidobenzol" conveys to the chemist an exact notion, not only of what body is meant, but of its construction. We might call such words "portmanteau words."

I make this introductory excuse for an attempt to explain, to those who do not know, the meaning and significance of the term "Enzyme." The definition of the word given in the *Encyclopedia Brittanica* is: "Enzyme (Greek ἔνζυμος leavened), a term first suggested by Kühne for an unorganized ferment, a group of substances in the constitution of plants and animals, which decompose certain carbon compounds occurring in association with them." Thus we get at once the fact that enzymes are connected with fermentation. The term fermentation was first applied to the process which leads to the formation of alcohol. The name arose from the copious evolution of gas, which accompanies the production of the spirit, and which gives the liquid in which it is taking place the appearance of a gentle ebullition.

* *Leather Trades'* Year Book, pp. 197–200, 1915.

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Cagniard de Latour about 1826 was the first to discover that alcoholic fermentation is caused by a definite organism—the yeast plant—but it was Pasteur who came to the conclusion that the execise of the fermentative power of yeast was connected with its nutrition in the absence of free oxygen. In 1833 the French chemists, Payen and Persoz, extracted a substance from germinating barley which was capable of liquifying starch paste, and in the process it formed a kind of sugar. This substance was clearly an unorganized substance, and at the same time, a ferment. On this account it was distinguished as an unorganized ferment. It was the first enzyme to be discovered, and was called by its discovers *diatase*. Two classes of ferments appeared to be thus indicated, the one a living organism, working only during its own growth and multiplication; the other consisting of substances which could be extracted by solvents from the cells in which they were formed, and capable of setting up decompositions apart from the life of such cells. The two categories were consequently called *organized* and *unorganized* or *soluble* ferments. The term *enzyme* is now generally used to indicate the latter class. According to Reynolds Green, we may consequently define fermentation to be the decomposition of complex organic material into substances of simpler composition by the agency either of protoplasm itself or of a secretion prepared by it.

The discovery by Buchner in 1896 of the enzyme *zymase* in yeast, which is capabe of fermenting sugar to alcohol and carbonic acid in a solution free from yeast cells, has caused us to abandon any distinction between the two classes of ferments, and the view now held is that all fermentations are the result of enzyme action.

Although a very large number of enzymes have been discovered—some hundreds—nothing is known of their chemical constitution. The sole means we have of recognizing and identifying them is their action on other substances. Fortunately this action is remarkable and extraordinary, so extraordinary indeed that we feel ourselves in the presence of a mysterious force beyond explanation by any of our present conceptions of chemical and physical science, I mean the problem of life. It is perfectly certain that life is largely carried on by the action of enzymes—they

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occur in the saliva (ptyalin) in the stomach (pepsin, rennin) in the intestines (trypsin, erepsin, enterokinase, lipase), and in the blood (thrombase, catalase). In the words of Prof. Bayliss: "The living organism is enabled by the use of enzymes to bring about, under ordinary conditions of temperature and moderate concentrations of acid or alkali, many chemical reactions which would otherwise require a high temperature or powerful reagents."

As an illustration of the properties of enzymes and the extraordinary powers of these bodies, the enzyme rennin, contained in the stomach, will coagulate 250,000 times its own weight of casein in milk. The action of many other enzymes is equally powerful, so that we see a very minute quantity of enzymes is capable of transforming a very large quantity of the body acted upon.

The enzymes which affect the tanner are mosty produced by bacteria, and are proteolytic in character, that is, they attack or digest the skin in putrefaction; milder forms exist in the limes, which dissolve only certain constituents of the skin. Enzymes also occur in the bran drench (diastase, invertase, cerealin). These, however, do not act on the skin, but on the starch of the bran. Enzymes are also the active agents in the puer or bates, and in this connection have formed the subject of various patents for artificial bates intended to replace the primitive and disgusting dung bates. In the tan liquors the enzyme tannase, discovered by Fernbach, ferments some of the tannins to gallic acid.

Prof. Procter in his "Text Book of Tanning," published in 1885, first pointed out that the process of bating is a fermentive one and attributed the principal action to bacteria. It was this statement which led the writer to begin an examination of the puer as used in a light leather works, and I take this opportunity of acknowledging the very great help and encouragement which I received from Prof. Procter, first by his letters, then by his personal advice and talk, in fact I look upon myself as one of his earliest students. A research on the mode of action of the dung bate in leather manufacture was begun in 1895, and in 1897 I succeeded in obtaining the active enzymes of dog dung in a fairly pure state, in the form of a light brownish powder. A solution of this powder containing 0.1 gram in 50 cc. water, di-

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gested boiled white of egg, blood fibrin, meat, etc., in a comparatively short time. When suitably combined with ammonium salts a very much weaker solution (0.005 gram per liter) will bring down skins in a similar manner to the original puer.

Röhm has proposed the use of an enzyme preparation for unhairing and bating skins in one operation. If such a process prove successful, the wet work of the tannery would be revolutionized. Lime and other alkaline depilatories would be abolished along with all the various processes for getting rid of them. The process still requires working out in practice, but enough has be n said to show in what way enzyme are of interest to the tanner.

BOOK NOTICE.

THE LEATHER TRADES' YEAR BOOK FOR 1915. Organ of the United Tanners' Federations of Great Britain and Ireland. Published by the Anglo-American Technical Company, Limited, 112 Tower Bridge Road, London, S. E.

This volume contains 212 pages exclusive of advertisements. The first 31 pages comprise membership lists of the Federations. Pages 32-51 are occupied with reports of committees. Statistics of various kinds occupy the next 57 pages. Then follow the papers listed below:

"Adulteration of Leather," H. R. Procter.
"Tests for Spent Tan Liquors," H. G. Bennett.
"Impressions of Dutch West Borneo," A. T. Hough.
"Purification of Waste Liquors," C. C. Frye.
"Army Sole Leather," James Randall.
"The Chemist in the Shoe Factory," J. A. S. Morrison.
"Syntans and Their Production," E. E. Wilkinson.
"The Available Tanning Materials," D. Woodroffe.
"Effect of the War on American Leather Industry," A. H. Lockwood.
"Dressing of Wool and Hair Rugs," H. Brumwell.
"The Elusive Warble," C. E. Parker.
"American Leather Trade and Hide Supply," John E. Wilder.
"The Chemist in the Tannery," L. E. Levi.
"The Hide and Allied Trades Improvement Society," E. Pim.
"Drum Tanning," E. Nihoul.
"The Tannery 50 Years Hence," J. R. Blockey.
"Solidification of Oils," M. C. Lamb.
"The Dyeing of Leathers in War Time," M. C. Lamb.
"Progress of Science as Applied to the Leather Industry in 1914," D. Woodroffe.

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ABSTRACTS.

Simple Test for Spent Tan Liquors. H. G. BENNETT. *Leather Trades' Year Book*, 1915, pp. 112-5. To determine whether any tannin remains in a spent liquor, filter it and add a solution of 1 per cent. gelatine and 10 per cent. salt. If there is no precipitate, the liquor contains no tannin, and by the amount of turbidity produced when a small amount of tannin is present, it is possible with some practice to estimate how much tannin there is. In order to judge of the acidity, to some of the filtered liquor add cochineal solution. This indicator turns red in the presence of free acids. With lime salts of weak acids it gives a black precipitate. The precipitate redissolves in excess of any acid. To 10 cc. of the filtered liquor add 3 or 4 drops of a 1 per cent. solution of cochineal. If a black precipitate forms, the acid in the liquor is so low that it is not fit to receive more hides. If a red color results from adding the cochineal, there is still acid enough to take care of the lime.

Army Sole Leather. JAMES RANDALL. *Leather Trades' Year Book*, 1915, pp. 136-42. The writer claims that there has been a steady improvement in the quality of boots served out to the British Army since Wellington's time, and that the extract tanned sole leather of to-day is wearing better than the straight oak tannage of 100 years ago. A still better leather as to wear and water resistance could be made "if the fetish of color were killed and buried once for all." The standard of color set in recent years has been so high that only by the use of mineral bleaches can it be reached, and that at the expense of the quality of the product. The practice of buffing soles is probably responsible for the demand that the color of the leather be light. In order to buff well, the grain must be scoured to remove the bloom, thus increasing cost and diminishing wear. The demand for an extract that would tan leather so that it would dry out light in color caused the French extract manufacturers to decolorize their extract with blood, etc., thus adding to its cost. The decolorized extract also makes a poorer wearing leather than the crude material. The writer regards it as an axiom that the more outer sole leather is improved in color with bleaching extracts, the worse wear the leather will give. A later development is the use of sulphonated oil on sole leather for improving color. The fact that the sulphonation is done by the use of sulphuric acid is regarded by the author as sufficient reason to condemn its use on sole leather. He anticipates the criticism "Tan your bends with crude extracts, use no bleaching extract nor sulphonated oil and don't scour, and the grain will crack unless you use a lot of oil or grease," saying that even so, the leather will wear better. He gives the results of his own experience in cross-country walking in the English Lake District, where much of the land is boggy. Several fellow members of the walking club also kept records. A summary of the evidence accumulated follows: (1) Tensile strength has little or nothing to do with wearing quality. Leather which was cracky on the grain,

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if properly damped before being put on the boots was more waterproof in wear than equally thick soles of fairly mellow grain, and also wore longer. (2) Leather that had been hammered by the shoemaker did not wear so well as that which was put on in the condition in which it left the tanyard. (3) Lightly tanned leather filled with grease did not wear so well as well-tanned leather filled with grease. Of course, the former had much the larger quantity of grease. (4) Unscoured leather gave better wear than scoured, finished in the same way. (5) Scoured leather wore better unbleached than bleached. (6) The use of sulphonated oil made the leather less waterproof. (7) Leather made from well-salted hides wore better than that from fresh slaughtered hides. The author's summary of conditions for best wear, water resistance and comfort in sole leather is: Use salted hides, do not use bleaching extracts, do not scour nor use sulphonated oil, pay no attention to color, fill with grease. In testing for cracky grain, do not bend to a sharper angle than the leather will be bent to in wear. The writer then takes up the subject of analysis. "Our friends the chemists are very fond of trying to lay down hard and fast lines as regards the amount of mineral ash, saccharine matters, soluble matter and fats which leather should contain. We should have more confidence in their judgment if they would give us wearing tests of leathers conforming to their ideals. Will any chemist say that a leather tanned solely with quebracho, and having 25 per cent. soluble matter will wear better than one tanned with chestnut and having 29 per cent. soluble matter? They may answer that the chestnut tanned piece would be better if it showed only 25 per cent. soluble matter. I doubt it. Even if proved so, could they guarantee to show conclusively what proportions of the different tans any leather contains? That is an important item, as some tans are much cheaper than others. The chemists, unless they are careful, will force tanners on to these cheaper tans, and so do a similar harm as the craze for light color did. Will chemists show us how to keep the saccharine matters down to 2.5 per cent. if we use crude chestnut extract? I think they will admit that crude chestnut extract makes excellent leather. Again, it can be proved that so late as January last leather submitted to two chemists was shown by their tests to contain 4 per cent. salts. The leather was tanned with extracts bought from firms with world-wide reputations, and great care was taken to see that it should be perfectly free from salts. The tanner is blamed, and told to use other extracts. I wish the analyst would tell him where he could get other extracts. As regards the amount of fat sole leather should contain, there is as yet no fixed limit, but there are rumors that 4 per cent. will be the maximum. I sincerely hope this will not be decided on, as, if so, any tanner may be convicted of adulteration because the greasy bends he makes (much to his own loss) contain, just where the official sample is taken, much more than 4 per cent.; in fact the average greasy bend contains 8 per cent. of fat in the greasy part. When shall we be free from these varying and unsound tests? Surely the great test of sole leather should be, as I have said before, wear resistance, waterproofness and comfort in wear. Until

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chemists can prove conclusively what tans have been used, and know the analyses these tans should show when used by the tanner on a commercial scale in the tanyard, both singly and in the various combinations (a large order I admit), and until some apparatus is devised that will subject leather to a test that will approximate to the wear a sole is subjected to on the average soldier's boot, I protest against the chemist's analysis being taken as conclusively showing whether sole leather is good or bad for the purpose for which it is to be used."

The Available Tanning Materials. D. WOODROFFE. *Leather Trades' Year Book*, 1915, pp. 151-3. Imports of oakwood extracts and valonia into Great Britain being stopped, and the supply of chestnut extract from France being diminished, tanners of sole leather in Great Britain are obliged to make substitutions. Some American chestnut is being received. The price of quebracho has advanced. Myrobalans and wattle are still available, the former of which can be used to good advantage in the earlier stages of tanning and the latter in the later stages. By judicious combinations excellent results may be obtained with these two materials. Wattle bark has heretofore not been much used by British tanners. Its reddish color and high astringency seem to have caused prejudice against it. It should not be used for dusting purposes, as it is liable to cause stains. The sugar content of wattle is low, so that when acid production in the liquors is desired, myrobalans, which supply sugar, may be blended.

Items from the Reports of Various Committees of the Tanners' Federations. *Leather Trades' Year Book*, 1915.

Mimosa Bark (Wattle).—As a result of correspondence with the Trades Commissioner for South Africa, mimosa bark is to be graded at the port of shipment as follows: Best heavy; second heavy; best light; second light; damaged and immature. The committee recommend that tanners demand a minimum guarantee of the tannin content of the different grades.

Leather Measurement.—The authorities of the National Physical Laboratory have tested various types of leather measuring machines, and issued a lengthy report. The machines have been found to be as accurate as possible. The error which may be expected in the Sawyer type machines is ¼ square foot, and in the pin-wheel type ⅛ square foot.

Iron Contamination in Sumac.—Members of the Federation were recommended to adopt the standard suggested by the I. A. L. T. C. As a result of correspondence with the Palermo exporters, considerable improvements are expected.

Under-curing of Frigorifico Hides.—Much dissatisfaction having been expressed in regard to the curing of S. A. hides, the matter has been taken up with the slaughtering and shipping firms, with good prospect of improvement.

Over-curing of Australian Dry-salted Hides.—Complaint is made that

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Australian dry-salted hides are more heavily cured and wetter than formerly. (Can it be that Australian shippers have found access to a supply of aluminum sulphate?—ED.)

Market Hide Classification.—It was decided that firsts should not have more than five visible warbles, seconds not more than twelve, and any number over twelve should constitute thirds or rejects.

The Elusive Warble. C. E. PARKER. *Leather Trades' Year Book*, 1915, pp. 161-8. Nearly all the matter of this paper is contained in the abstract given on pages 196-200 in this JOURNAL for April last.

The Hide and Allied Trades Improvement Society. E. PIM. *Leather Trades' Year Book*, 1915, pp. 175-9. The aim of this society is to place on a more sound business basis the conditions of sale and the manner of handling hides taken off animals killed in Great Britain. A Central Committee has been established in London, and District Committees formed in Bristol, Birmingham, Leeds and Manchester. Each of these committees has a travelling inspector, who is under the control of the honorary secrtary of the district to which he belongs. If any buyer or seller has any fault to find with the inspector or his work, complaints or suggestions must be made to the honorary secretary, who, if he thinks it necessary, will then instruct the inspector. This plan enables the inspectors to avoid discussions with buyers or sellers. Each inspector makes a weekly report to his secretary in duplicate, the duplicate copy being sent to the Central Committee. At committee meetings the inspectors attend so that members may ask questions. The reports are absolutely private, and neither the inspectors or secretaries are at liberty to show them to any one. If there is trouble in any market, it is the duty of the secretary to take the instructions of his committee as to what shall be done. When the authority of the District Committees is called in question, reference is had to the Central Committee, whose decision is final and binding. The society has provided or loaned stamping hammers of uniform size to nearly all the hide markets, definite letters being assigned to each dealer. In nearly all cases these letters are associated with a circle for firsts, with two horizontal lines for seconds, and with three vertical lines for thirds, so that in taking in hides, a foreman can tell at a glance to what grade each has been assigned. The stamping is done on the flesh side at the root of the tail.

The Dyeing and Staining of Leathers in War Time. M. C. LAMB. *Leather Trades' Year Book*, 1915, pp. 201-5. Good reds may be obtained by the use of Brazilwood and sulphate of alumina, drumming in the dye solution, and then adding the mordant to the same bath. A brighter color is obtained by adding a little titanium sodium oxalate. Pale greens may be produced with indigo extract and fustic extract, using alumina sulphate as a mordant. Browns are made with Brazilwood extract and

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fustic, mordanting with bichromate of potash. Adding titanium oxalate gives yellows. Logwood and titanium oxalate give good blacks. Addition of a small amount of aniline color improves the result, however. Tan browns may be obtained with gambier and titanium, modified with Brazil or other redwood extract. Logwood and alum give good purple shades, fustic and alum pale yellows, fustic and titanium deeper yellows. Brazil or peachwood, alum and titanium give scarlet reds, brighter if fustic be added. Good dark browns can be obtained with gambier. Brazilwood, bichromate and titanium oxalate. Annato may be used for pale yellow shades.

A Modification of the Hertzfeldt-Bohme Method for the Detection of Mineral Oil in Other Oils. F. P. VEITCH AND MARION G. DONK. *Bureau of Chemistry Circular No. 85.* The experiments described relate to the detection of mineral oil in turpentine. As little as 2.5 per cent. may be detected. The turpentine is mixed with 38 N sulphuric acid, and the amount of residue observed, as well as its index of refraction. Babcock milk tester bottles are used, 5 cc. of turpentine being poured slowly into 25 cc. of the acid, with constant agitation, the bottle being immersed in ice-water to prevent the temperature from rising above 65° C. After thorough mixing, the bottle is filled to the top of the scale by pouring in more 38 N acid, and either whirled or allowed to stand over night. Pure turpentine leaves a negligible residue, and with carefully standardized conditions, and residue found may be calculated to the percentage of mineral adulterant.

Determination of Melting Point by Thermometer Bulb Method. ROBERT MELDRUM. *Chem. News,* 108, 223-4. Errors in this method are ascribed to faulty manipulation. The apparatus recommended consists of a tall beaker 7 x 3 in. filled with water and fitted with a bung through which passes a 7 x 1 in. test tube in which is placed the thermometer with its bulb coated with the melted fat. Around the test tube is a plunge stirrer. The most important point in the procedure is to obtain a coating of the right thickness, which is tested by first taking a rapid dip in and out the fat melted about 10° above its melting point, cooling about 10° below, determining roughly the melting point; if the first drop to form is opaque the coating is too thick and if the first hangs too long or a second fails to appear it is too thin. The thermometer is now cleaned, heated or cooled 5° or 10° from its initial temperature, dipped, and another determination made, and so on until the right thickness is obtained. Two drops should form. Viscosity plays a very important part, and for the rate of heating near the melting point 1° per 2 minutes is not too slow. Among 49 determinations given the maximum variation did not exceed 0.6°. The differences from the actual melting points were not determined, but the results with stearic acid and spermaceti were apparently well within 1° of the true melting point.

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PATENTS.

Tanning Material and Process of Preparing the Same. U. S. Patent 1,147,245. HENRY HICKS HURT, assignor to Robeson Process Co.

A concentrated sulphite waste liquor preparation is first treated with sulphuric acid in amount sufficient to precipitate the major portion, but not all of the lime present, and is then treated with a soluble bisulphate in amount sufficient to precipitate substantially all the remainder of the lime present in the liquor. The tanning extract thus obtained contains free lignosulphonic acid or acids but substantially no free mineral acid, being acid to litmus and phenolphthalein, but substantially not acid to Congo red.

In the manufacture of wood pulp for paper making purposes by the so-called sulphite process, comminuted wood or other cellulose material is digested with solutions containing bisulphites, such as bisulphite of calcium or a mixture of calcium and magnesium bisulphites, usually with some free sulphurous acid, until the soluble or non-cellulosic constituents of the wood, which are usually grouped under the broad term of "lignones," are dissolved, leaving substantially pure cellulose to be subsequently worked up into paper stock. The exact nature of the compounds formed by the interaction of the soluble lignones of the wood with the bisulphites present in the digesting solution is not well understood, but it is generally believed that said compounds are, or are in the nature of, lignosulphonates of the bases employed; that is, salts of what are by common consent usually termed lignosulphonic acids. These socalled lignosulphonic acids, when in free or uncombined condition, are highly efficient tanning agents, being particularly useful for their plumping effect. In the liquor as it comes from the digesters, however, these lignosulphonic acids are largely combined with lime, and the presence of this base is very disadvantageous in a tanning extract both because of its injurious effect on the hides to be treated, and also because it serves to hinder and prevent the activity of the lignosulphonic acids as tanning agents. The problem is therefore to get rid of the lime, to set free a large proportion of the lignosulphonic acids, and to produce a concentrated tanning material containing as high a percentage of tans and as low a percentage of non-tans as is possible. It is also important that the finished product shall contain substantially no free mineral acids such as sulphuric acid, since any free sulphuric present in the tanning extract will inevitably result in a poorly tanned leather which deteriorates with great rapidity. Free mineral acid also produces excessive plumping of the hides.

The raw sulphite waste liquor coming from the wood digesters is a rather dilute solution of lignosulphonates, largely lime lignosulphonates, and is of comparatively low specific gravity, being ordinarily in the neighborhood of from 2° to 6° or 7° Baumé, or thereabout. It is also acid in reaction, often containing free mineral acid. For the purposes of the present process in its most advantageous form, this raw sulphite waste liquor as it comes from the digesters is not suitable starting material

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to employ. If, however, this raw waste liquor be first suitably neutralized with lime, and particularly with a dolomitic lime, and the liquor thus neutralized be then evaporated down in vacuo, a concentrated product of a specific gravity of about 31° or 32° Baumé or thereabout may be obtained which is eminently suitable as the starting material for the present process. Such a concentrated liquor is substantially neutral, is normally very viscous, and contains generally in the neighborhood of 2 per cent. combined lime (CaO).

It has been proposed heretofore to remove the lime from sulphite waste liquor by means of sulphuric acid alone, or by means of a soluble bisulphate alone, either the sulphuric acid or the bisulphate when added to the sulphite waste liquor producing calcium sulphate which being relatively insoluble is supposed thereby to be precipitated out. It has also been proposed to treat raw sulphite waste liquor as it comes from the digesters with sulphuric acid in conjunction with sodium bisulphate, the amount of sodium bisulphate used being relatively large compared to the amount of sulphuric acid. None of these proposed methods is found to work satisfactorily in practice for reasons given below.

In order to obtain a satisfactory tanning extract from sulphite waste liquor, it is very important that the process be conducted in such a manner that there is no necessity for further treating the product after precipitating out and removing the lime. If sulphuric acid or an alkali bisulphate, or both, be added to raw or unconcentrated sulphite waste liquor in the proper theoretical proportion to remove the lime and thereby also to set free a certain proportion of lignosulphonic acids, it is found upon concentrating the treated waste liquor that an acid is inevitably developed during the evaporating process which acts like and probably is sulphuric acid, some of this acid combining with traces of unprecipitated lime still remaining in the liquor to precipitate lime sulphate, while the greater proportion of the acid thus developed remains free, giving the final concentrated product a very decided acid reaction toward the indicator Congo red, thus indicating the presence of a mineral acid. Such a product is ordinarily undesirable for use in tanning leather, hides or skins for the reasons that the sulphuric acid remains in the finished leather and ultimately rots it.

It has also been found that it is impractical to treat a concentrated sulphite waste liquor product with sulphuric acid alone to precipitate out the lime. It is, of course, very desirable not to diminish the specific gravity of the concentrated sulphite waste liquor preparation any more than is absolutely necessary in precipitating out the lime. Consequently in using sulphuric acid as the precipitant, it is highly desirable to use it in a form of strong commercial acid of say 60° or 66° Baumé gravity. It has been found, however, that if the theoretical quantity of acid of this strength be added to a concentrated sulphite waste liquor preparation, the acid does not all combine with the lime, but a substantial proportion thereof attacks the valuable lignosulphonic constituents of the liquor, decomposing and carbonizing or burning them and thereby greatly reducing the per-

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centage of tans in the finished product besides materially deepening its color. Furthermore, where the full theoretical quantity of sulphuric acid is added, even if special precautions be employed to lessen the decomposing and burning action just described, a certain reaction always occurs in which a considerable amount of finely divided or colloidal free sulphur is liberated, together with sulphurous acid, this sulphur rendering subsequent filtration of the liquid extremely difficult and expensive. Apparently it is only the later portions of the sulphuric acid thus added which act in this undesirable way. The first portions of acid added react selectively or preferentially with the lime compounds in the liquor to form lime sulphate, which is precipitated out, and to see free lignosulphonic acids. As soon as the proportion of lime compounds remaining in the liquor is reduced below a fairly definite point, the selective action of the acid on the lime compounds seems to cease, and the acid then begins its described attack on the valuable organic constituents of the liquor with liberation of sulphurous acid and free sulphur. If, on the other hand, a soluble bisulphate alone be employed to precipitate the lime from a concentrated product of the character described, while the disadvantages of burning out the tanning constituents and liberating sulphur, etc., are avoided, nevertheless an equally objectionable effect is produced by the introduction of a large quantity of soluble non-tans in the final product; that is, sodium salts of lignosulphonic acid are formed which have comparatively little or no tanning effect, and are not absorbed by hide powder to any material extent, and which serve thus merely to increase the "ash" content of the tanning extract.

According to the present invention the above difficulties are avoided by a novel method of reacting under carefully controlled conditions upon a neutral or even slightly alkaline concentrated sulphite waste liquor preparation of the general type obtained by neutralizing raw waste liquor with lime and evaporating. In practice such a preparation of approximately 31° to 32° Baumé specific gravity is treated with strong commercial sulphuric acid in amount somewhat less than that theoretically necessary to remove all the lime. The acid should be added while stirring or otherwise agitating the liquor and it is well to have the liquor somewhat warm. By using the amount of acid specified and by operating under proper conditions of agitation, this addition of acid produces no decomposition or burning of the organic constituents, and no liberation of sulphur or sulphurous acid to an undesirable extent, practically all of the acid reacting with the lime compounds of the liquor to precipitate out calcium sulphate. After the sulphuric acid has been thoroughly mixed with the liquor, the necessary amount of an alkali bisulphate, advantageously sodium bisulphate, which has been first dissolved in the least possible amount of water, is added to the mixture, this amount being approximately just sufficient to remove the combined lime still remaining in solution. The whole mixture is then best thoroughly stirred for several hours, whereupon the liquor is drawn off and filter pressed to remove the precipitated matter, chiefly calcium sulphate. The liquid

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product thus obtained contains a large proportion of free lignosulphonic acids together with a relatively small proportion of lignosulphonates of soda derived from the sodium bisulphate employed, but contains substantially no lime salts and no mineral acid. The roduct reacts acid toward litmus and phenolphthalein, but non-acid to Congo red or in rare instances only faintly acid.

A material possessing a somewhat greater percentage of tanning material for the same concentration may be made by first fermenting away the sugars contained in sulphite waste liquor, thereafter concentrating to the desired degree and treating as above described.

Chrome Liquors. British Patent 7467. F. HIRSH, Vienna.

Bichromates are reduced with a mixture of aluminium sulphate and sodium sulphate.

Composition for Tanning Hides and Skins. U. S. Patent, 1,147,178. MARTIN B. LARSON, Molson Washington. A mixture of gambier, common salt and epsom salts.

Rotary Drum for Tannage. British Patent 7762. E. HAWTHORNE, Liverpool.

Tanning Process. U. S. Patent, 1,149,298. W. S. SHAW, Boyne City, Michigan. The hides are immersed in liquors contained in vessels in which a high vacuum can be maintained. The liquors are boiled intermittently, the vacuum being so high that the boiling temperature is too low to injure the hides. Apparently the scheme is similar to that of the Nance patent.

Process of Preparing and Packing Tan Bark. U. S. Patent, 1,146,963. W. S. SHAW. Boyne City, Michigan. The bark is removed from the tree by machinery which shreds it; then dried and put up in very highly compressed bales.

Machine for Treating Hides or Leather. U. S. Patent, 1,147,098. S. H. Kehrhahn. Frankfort, Germany.

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John H. Yocum has been appointed Chairman of the Committee on Disinfection of Hides, in place of W. K. Alsop, resigned.

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VOTE ON PROVISIONAL METHODS.

The proposed methods for moellon analysis and for the examination of hard greases were voted on as provided by the By-Laws. Twenty-three votes were cast. The moellon methods received 21 affirmative votes, 2 votes were negative. In the case of the proposed methods for hard greases, there were 19 affirmative and 4 negative votes. The number necessary to adopt is 16. Both methods are therefore adopted.

THE "ADULTERATION OF LEATHER."*

By H. R. Procter, M.Sc., F.I.C.

The industrial chemist, like the father confessor, gets sidelights on the morals of his clients; and, though the individual cases are strictly under the seal of the confessional, a few general observations are permitted. Successful sole-leather tanners, like the rest of the world, may be roughly classified into the honest and the dishonest, the distinction between them being that while the former weight their leather with tanning extracts only, the latter permit themselves the use in addition of small quantities of glucose, dextrine and mineral salts. There is also an intermediate class who employ ready-prepared "finishing extracts," "asking no questions for conscience sake."

To the buying public, including the war office, the distinction between the "honest" and the "dishonest" is of little moment. All tanners are in business either to make profits, or from "the force of circumstances beyond their control," and in either case the necessary condition of survival is to make the greatest possible quantity of leather out of the least possible quantity of hides, since this is much the most costly constituent. Modern rapid processes necessitate the use of tanning material in considerable excess of that actually required to convert the hide into leather, so that a certain amount of what from the buyer's standpoint is really "loading" must be accepted as unavoidable, but it should not be excessive, and probably 10, and certainly 25 per cent. would cover all that is actually justifiable, while the larger amounts,

* *Leather Trades' Year Book*, 1915 pp. 109–11.

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which are quite common are, in the writer's opinion, just as much adulteration as if some entirely foreign substance were employed.

The moderate excess of tanning matter which has been suggested is not wholly useless to the buyer. In modern rapid processes the hide is rapidly saturated by the excess of tannin, but its actual diffusion into the fibers themselves is necessarily slow; and it is probable that changes analogous to those which take place in the "aging" of alumed leathers also occur in rapid vegetable tannages, leading not only to the more complete penetration of the fibers, but to a portion of the originally soluble tannins gradually becoming insoluble by oxidation and other changes, and so increasing the solidity and water-resisting properties of the leather. If some form of "adulteration" could be invented which would have the same permanent filling and solidifying effect, without in other ways injuring the quality of the leather, its use, whether "honest" or not, would be wholly advantageous to the public. Such a method is probably not beyond the resources of modern chemistry, and indeed the water-proofing of chrome and vegetable leathers with solid waxes, though really advantageous in use, constitutes a very heavy "loading" with quite cheap materials, and should enable the leather to be sold at a considerably lower price per pound.

The effect of loading, either with extract or other things, is to make the leather apparently both firmer and thicker. The wear of a properly tanned leather is largely proportional to the actual leather fiber which it contains, so that heavy loading with soluble materials is a double fraud on the purchaser. In this connection it may be worth while to remark that the chrome tannage, while preserving the fiber very completely, is at best an empty one, and even after waxing is far from having the thickness or weight which the same hide would have if vegetable-tanned, though its wear may be decidedly superior. It is, therefore, a mistake to ask for the same standard of thickness, which can only be obtained by the use of heavier and more expensive hides. The chrome process is actually a cheap one, hide for hide, and the only reason why chrome sole should be dear is because of its comparative thinness and light weight.

As regards remedies for loading, it seems to me that they lie, as

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always, with the buyer. He has only to demand a guarantee that the solubles should not exceed a fixed reasonable percentage, and to pay such a price as will cover the difference between the cost of dry extract and finished leather, and by most of the trade he will be honestly served. If at the same time he would abate his excessive demands for a useless paleness of color he would obtain a better and more durable leather for his money, since all bleaching processes reduce the water-resisting qualities of the leather, and the present supply of available tanning materials renders it impossible to produce by direct tanning the pale yellowish color formerly in vogue, except by the sacrifice of other and more important qualities.

It may be asked how the buyer is to satisfy himself that he is really getting the proportion of actual leather which he is paying for, since a complete leather analysis is necessarily expensive. I would reply that the main point is the percentage of solubles, and that this can be determined with fair accuracy by anyone. The simplest way is to cut two samples of approximately equal weight, of which one serves merely as a standard and check on drying. The other is soaked—for some hours in tepid water—say of 100°-110° F., gently bent and kneaded to facilitate the washing out of the soluble portion, and thoroughly dried alongside the check-sample, which should not materially lose in weight, or of which the loss must be deducted from that of the washed portion. Such a process will not merely show the loss of weight on washing, but will give a good idea of how far the apparent firmness is due to the matters washed out. A mere determination of solubles in the laboratory is not an expensive matter, but specially water-attracting matters like salts and glucose should be absolutely prohibited in army contracts, and of course must be tested for individually.

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THE TANNERY OF FIFTY YEARS HENCE?*

By J. R. Blockey, M.Sc.

In these days of rapid changes, when industries are gradually falling under the sway of applied chemistry, and when science is becoming the mistress rather than the servant of industrial processes, and bringing revolutionary methods in its train, it may seem a bold thing to prophecy 50 years ahead, even in such a conservative industry as that of leather making.

One can have no correct vision of what will be current in 50 years, but it should be possible, by examining the changes and progress made in the last 10 or 20 years, and by a process of extrapolation to determine the lines on which future progress and changes will be made.

The surface of the science of leather manufacture has only been scratched, and underneath there are untold problems to be solved. The problems which have already been solved give an indication of what lies under the surface and the nature of the remaining problems.

Some of the main lines along which progress is likely to be made are:

(1) The replacement of hand labor by machinery.

(2) The conservation of raw materials and the utilization of by-products.

(3) The introduction of new materials.

(4) The replacement of rule of thumb methods by organized scientific methods.

Running concurrently with these lines and dependent upon them, there will be a great shortening of time, and much more economical methods of manufacture. In the space at disposal here it is impossible to give a detailed account of the progress likely to be made on each of the above lines—a general outline or a typical case must suffice.

(1) *The Replacement of Hand Labor by Machinery.*—The leather industry will be no exception to the general increase in the application of machinery. Although leather was made before machinery existed, the latter has rendered possible the present wonderful variation in effects obtained upon the skins of animals.

* *Leather Trades' Year Book*, 1915, pp. 186–93.

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Apart from detailed improvements in existing machines, it is probable that the whole disposition of the machinery in the tannery will undergo changes. It seems likely that with the introduction of electric motors, it will become more and more common to run each machine independently, so that there will be greater economy in power production by doing away with long shafts and countershafts running empty. A local breakdown also, will not entail a dislocation of the entire plant.

Much of the manual labor which is now used for the heaviest and dirtiest work, such as hauling hides from limes, will probably be replaced by machine hauling plants, and it is quite possible that with new methods of beam-house work (touched upon later in this article) the amount of hauling will be considerably reduced. The American method of liming in warm liquors, and depilating in the drum, gives an indication of labor saving. With the advent of successful unhairing and fleshing machines, the heavy labor formerly necessary for these processes will be disposed of, and instead will be available for lighter and more congenial work.

Methods of tanning will rely more and more upon mechanical aids, such as drums and paddles, partly because the length of time will be reduced, and partly because the tannages used will be largely chemical and will depend upon motion. This will cause an increase in the amount of machinery and a change in the arrangement of the tannery.

(2) *The Conservation of Raw Materials and the Utilization of Waste or By-products.*—That there has been and still is enormous waste of raw material, both in connection with hides and skins and with the materials employed to convert them into leather, will scarcely be disputed, but signs are not wanting that the significance of these losses is being realized, and steps taken to remedy them. The work of the International Commission for the Cure, Preservation and Disinfection of Hides and Skins, shows that the first half of the question is receiving attention.

Many of the losses incidental to raw hides and skins are entirely preventable. With the knowledge of the true life history of the warble-fly and its grub, the elimination of warble holes, with the attendant enormous loss of value to the flesh, milk and hide of the animal, should only be a matter of time. Branding,

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goad marks, bad flaying, etc., could also be eliminated. The improved methods of marketing, cleansing, and sterilizing of raw hides and skins would enhance the value of leather forming substances enormously, by preventing salt stains, by increasing the ratio of first selections to seconds, and by giving more actual leather.

The preservation and utilization of the other class of materials used in making leather, that is, all those except the hide and skin, also offer great possibilities. The loss of tanning matter caused by (*a*) incorrect methods of leaching raw materials; (*b*) wasteful methods of working liquors; (*c*) the use of unsuitable water; (*d*) unnecessary fermentation, is probably much greater than is generally realized. To take the last point only, tanners allow liquors to ferment so as to produce acids—but the nature of the acids produced is quite hypothetical, whilst tanning matter is much more expensive than acids, which can be added artificially in controllable quantities and kinds.

Places where losses which are small, but which are appreciable when considered over a fair length of time, occur, are numerous; acids, dyestuffs and soaps, are all wasted by the use of hard water. The utilization of waste products has, in many industries, been the salvation of the process. The classical example is that of the Leblanc process of alkali manufacture, which would have been completely ousted by Solvay's process, had it not been for the commercial value of the by-products in the former case. Perhaps the most striking instance of this in the leather trades is the utilization of the spent tanning material for the formation of producer gas for power plants.

There is an additional incentive in the tanning industry to utilize waste products, in that these are largely putrescent and have to be treated or purified in some way so as to fulfil the conditions laid down by the sanitary authorities for trade. It is quite possible that many of the waste or almost worthless products of a tannery could be utilized for some purpose and thereby made valuable.

(3) *The Introduction of New Materials.*—Perhaps the greatest developments in the manufacture of leather will be in con-

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nection with the materials, and incidentally, with the methods employed.

(*a*) *Enzymes.*—The universal process for the removal of the hair, *i. e.*, liming, together with many of the incidental processes, such as bating and drenching, may possibly be replaced by much simpler, quicker and more controllable processes, involving the use of enzymes. It is well known that the actions during liming, puering and drenching are dependent upon the growth and multiplication of bacteria. It is impossible here to describe in detail the mechanism of the reactions which occur in these processes, but it may suffice to say that most of the changes are brought about by the decomposition products of the bacteria, called enzymes, and the products of the enzymes. Enzymes are formed during the growth of living cells or organisms. They are extremely complex in composition. One important feature is that a small quantity of an enzyme is capable of decomposing a large quantity of the material upon which it acts. In this sense the behavior is like the inorganic catalysts. There are all sorts of enzymes capable of producing all sorts of effects. One enzyme will decompose proteids (trypsin) while another will split up fats (steapsin).

In the various processes in the beam-house, during the removal of the hair, and in the "pulling down" effects of bating and drenching, the changes are largely those which enzymes are capable of affecting, *e. g.*, in liming, the effect is mainly a proteolytic one, or proteid splitting action, in which the proteid composing the epidermis and the hair roots, is decomposed and liquified, so that the hair is loosened. In addition, there is a fat-splitting action, in which the fat is saponified, so that it can be removed by scudding.

The enzymes which bring about these changes are evolved by the growth of bacteria in the liquors. One enzyme is usually only capable of producing one effect, but by combining one with another, or by using several, it should be possible to produce any combined effect desired. In the usual processes of liming, etc., the formation of these enzymes is left to chance, and it is quite probable that many undesirable effects, such as the solution of

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leather-forming hide substance, take place along with the necessary ones.

These enzymes can be separated from the living cell, purified, and kept in the purified condition for considerable lengths of time without losing their powers. By taking therefore, definite quantities of these known substances, it is possible to gauge and foretell the extent of their action and the effect on the pelt. It is not likely that one enzyme will take the place of all the processes of liming, deliming, bating and drenching, but it should be possible to combine several enzymes to produce the sum-total effect of all these processes in one operation. Naturally one combination will not suffice for all classes of leather, which require such different beam-house treatment; but by experiment it should be possible to blend them in suitable proportions to produce the different effects.

The effect of such a process would be revolutionary: (1) the whole of the preliminary wet work, which now occupies so many processes, would be accomplished in a single operation; (2) The length of time of this wet work, *i. e.*, before the hide goes into tan liquors, and during which the hide is in a putrescible condition and liable to undergo damage, would be considerably shortened; (3) The process would be carried out in sterilized liquors without unnecessary loss; (4) The whole process would be almost odorless and certainly free from the disgusting nature of the present-day processes; (5) The effluent question would be greatly simplified; (6) The nature of the subsequent tanning operations would have to be altered and perhaps simplified; (7) The ever-present and vexed question of "Why do we lime?" would not exist.

This is no philosopher's dream, for practical experiments have shown it to be possible and successful. The possibilities of the use of enzymes are almost unlimited. It has been suggested more than once that a successful degreasing process could be elaborated by the use of enzymes. There are well known enzymes which possess the property of saponifying fats. By combining these in sufficient quantities with those used in the preliminary depilating process, it would be possible to remove the natural grease, but it is scarcely likely that enzyme degreasing would

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entirely take the place of a modern degreasing plant which has special uses on tanned leathers.

Before such an exclusive use of enzymes becomes common, many new materials will be suggested for the different beamhouse processes. Every few weeks sees some new deliming, bating or puering material placed in the market.

(*b*) *Tanning Materials.*—The number of materials which can be made to produce leather is legion and is being added to continuously. Prof. Procter's dictum that almost anything will make leather is being realized. Lack of space forbids a description of materials which seem to have commercial possibilities (and many of those new materials which are suggested have none) but there is one class of material which calls for special comment, *viz.*:—the synthetic artificial tannins. Until the composition of the tannins present in raw materials is known, and until the correct theory of tanning is solved, the nature of the tanning process will be largely empirical, but with the knowledge of these two things the process could be conducted on quantitative and scientific lines. At present one cannot say why the tannins—say of sumac and valonia—produce such different leathers, but with the above knowledge, not only would it be possible, but other problems would be solved. The effect of any material could be much more easily modified, the saving of material would be enormous, the length of time might be reduced (and with less disastrous results than some of the present attempts at quick tannage).

A step in this direction is the production of the synthetic tannins, the composition of which is known, and which can be modified, to produce different effects. When the conditions which govern the combination between hide and tannin are known, the possibilities of these synthetic tannins will be further widened. Something similar to what has been described in connection with enzymes will be possible. By blending the different synthetic tannins, different effects could be produced, the leather could be made light or heavy weighing, firm or mellow, at will. The whole process of tanning would be simplified, because the causes of the changes in the pelt would be known. Instead of present methods, in which quantities and strengths of materials are empirical, and in which it is quite possible that many changes occur which are un-

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necessary and wasteful, but which must accompany the necessary ones; with materials of known composition, the reactions would be much more quantitative, resembling simple chemical reactions. The quantities of material required could be calculated beforehand, so that there would be none of this present enormous excess of tanning matter. The use of leaches, of strong liquors and of lay-away pits, in all of which, wasteful and unknown changes occur, would be replaced by simple liquors of definite composition.

The preceding consideration has only dealt with the so-called vegetable leather, but it seems likely that the present popularity of the mineral tannages, particularly the chrome tannage, will extend. This is not the time or place to discuss the merits or demerits of chrome leather, but there is no doubt that increasing quantities are being made, and what has been achieved with one mineral tannage may be possible with other tannages, of which many have promise. The gradual replacement of the ordinary methods of tanning by mineral and synthetic tanning processes, will alter the disposition of tanneries and workshops. The long series of pits will give place to fewer ones, along with mechanical aids to tanning, such as paddles and drums. It will be possible to produce greater quantities of leather with much less floor space, and the ratio of turn-over to capital will be increased.

With the use of new materials and methods, new kinds of leather will be made. Although the popularity of these will follow the dictates of fashion (an example of this can be seen in the different shades and kinds of leather used in ladies' handbags and fancy shoes) the special characteristics of the new leathers will open out new possibilities, and widen the sphere of use. (The special wear-resisting qualities of chrome leather have made it possible to utilize it in the making of combination motor tires, a purpose for which vegetable leather would be useless.) Everything points, therefore, to a widely increased scope for the uses of leather, for apart from new uses, the substitution of other materials for many of the present day uses of leather has not proved successful.

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DRESSING OF WOOL AND HAIR RUGS.*

By Harold Brumwell.

It is a well known fact that all skins which have been dressed by the alum and salt process are very much affected by atmospheric changes. During damp weather the amount of water which the skin absorbs is sufficient to give quite a wet and unpleasant feel. Skins which are affected in this manner are far from pleasant when used as rugs for domestic purposes. When the skins are washed, as white ones repeatedly have to be, a considerable amount of alum is washed out and the skin dries out hard and horny, and must be redressed in order to bring it back to a satisfactory condition. This process is not easily performed except by those people possessing considerable experience in the methods employed. The use of "Neradol D" as a substitute for the alum process has proved very satisfactory; the skins have a very fine white and soft flesh, are not subject to atmospheric changes, and may be washed quite easily without any detrimental effect on the skin. The details of the method which are given in the following account have been worked out in the Leather Department of the University of Leeds, and involve the use of "Neradol D." This material is no longer available, but as many "Syntans" are at present being manufactured, no difficulty should arise in finding a substitute, although the writer is not able to say from experience what the results are with the substitutes which are already on the market.

Soaking and Washing.—If the skins are in a dry condition they are soaked in fresh cold water in a pit, great care being taken that putrefaction is entirely avoided otherwise the hair or wool will slip. The use of alkaline softening agents, such as sodium sulphide or caustic soda, which in very dilute solutions are sometimes recommended for softening hides, must in this case be avoided, as they have a tendency to slightly damage the hair. Copper sulphate (2 ounces for 30 gallons) may be used as a germicide during the soaking process. Dried skins usually require about 36 hours to soften; fresh skins should remain over-night. If the skins are very dirty, a change of water is recommended. After soaking, the goods should be well worked on the flesh side,

* *Leather Trades' Year Book*, 1915, pp. 157–60.

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any superfluous flesh being removed, and they should then be run in the wash wheel for 20 minutes.

The skins are now given a further washing for 1 hour in a solution of 1 per cent. borax and 2 per cent. soft soap, which very effectively cleanses the wool or hair. The soap and borax is removed by running in water in the wash wheel for 5-10 minutes.

Liming.—The Pullman-Payne process of liming, as originally described, was first used, but it was found that by immersing the skins in the caustic soda solution a "singeing" effect was produced, and the hair or wool became brittle. The following modification of the original process works very satisfactorily. A solution of 1½ per cent. of caustic soda is made into a thin paste by the addition of French chalk, china clay, or some inert material of this description. This paste is applied to the flesh side, the skins folded up, flesh in, and allowed to stand 4-5 hours. They are then thrown into a 4 per cent. solution of calcium chloride (4 pounds calcium chloride per 10 gallons of water) and left several hours, usually over-night. The skins should then be washed in water in the drum, and delimed with acetic or lactic acid. About 4 ounces of lactic acid (32 per cent.) per dozen skins will usually be found sufficient, but a slight excess of acid will do no harm. The skins are now ready for tanning.

Tannage.—The tannage, which takes place in the drum, is commenced in a 2 per cent. "Neradol" solution (2 pounds Neradol per 10 gallons water) the strength being gradually increased from time to time by the addition of "Neradol," until a 5 per cent. solution has been reached. The tannage usually occupies about 2 days. The solution having reached a strength of 4 per cent. on the first day, is strengthened up to 5 per cent. on the morning of the second day, and the goods drummed until night, when they are taken out and drained over-night.

Finishing of Sheepskins.—It will be found in the case of sheepskins that fat-liquoring is unnecessary, as the skins usually contain sufficient, and sometimes too much, natural fat. To get rid of the excess fat, the skins, after drying, are coated with a thin paste of whitening and water on the greasy parts of the flesh and are then put into a hot drying room. The temperature should

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be high enough to melt the fat so that, as the water evaporates from the whitening, the fat takes its place. When quite dry the whitening should be scraped off, and the process repeated, if necessary, until all the grease is got rid of.

The method suggested by A. Seymour-Jones (*Collegium,* p. 620, 1912) for the removal of grease from butts, was used on sheepskins with satisfactory results. The skins were drummed in a 5 per cent. solution of "Hypo," and after a short period a little acid was added and drumming continued. The amount of acid used was less than ¼ per cent. of ordinary commercial hydrochloric acid. This method proved very satisfactory, but it might be advisable to increase the quantity of "Hypo" to 10 per cent. or even 20 per cent. with very greasy skins; of course the acid should be increased in the same proportion. The skins should now be dried, damped in sawdust, staked by hand staker, fluffed, and the wool well combed.

It has so far proved rather difficult to dye Neradol tanned wool skins, but recently satisfactory blacks have been produced as follows:—The skins were drummed 3 hours in 0.5 per cent. solution of copper sulphate and allowed to remain in this solution over-night. They were then drained and placed in a shallow dye-bath containing 60 grams Furrol S crystals (Cassella), 10 grams phenylene diamine (Cassella) dissolved in 2 gallons of water with 35 cc. hydrogen peroxide. Care was taken that the goods were fully immersed, and they were allowed to remain in this solution over-night. The skins, after washing, were dried and finished as above.

Finishing of Springboks, Deer Skins, Etc.—The skins after tanning are fat-liquored with sulphonated oils, soaps on no account should be used, as this will lead to the liberation of free fatty acids, owing to the nature of the Neradol tannage. A mixture of 4 per cent. sulphonated castor oil and 4 per cent. moellon (per cent. on leather weight) has proved very satisfactory. Sulphonated cod oil substituted for the castor oil gave a very soft and full feel, but the objection to this is its smell, which is not very pleasant on mats used in a warm room. The skins are dried, damped back in sawdust, staked and fluffed. If the hair feels at all oily the skins should be run in either dry

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sand or sawdust in a drum, this will remove the grease and at the same time polish the hair.

An experiment on Springbok skins was recently made where the tannage was carried as far as the stage of a 4 per cent. solution of Neradol, the goods were then removed, drained, fat-liquored in a mixture of 2 per cent. sulphonated castor oil, 2 per cent. sulphonated cod oil, 1 per cent. whale oil (on the skin weight), returned to a 5 per cent. Neradol solution in which the tannage was finished. A second fat-liquor was given as before, but increasing the whale oil to 2 per cent. The result of this process was to give a leather with a good deal of stretch, resembling more the effect aimed at by the furrier in the oil tannage.

It will be noticed in the above account that the tannage has been carried out in every instance in the drum, using about 30 gallons for half-a-dozen skins. One would have anticipated that felting would take place in the case of sheepskins, but although very many skins have been done in this manner, no felting effect has been observed. In no case were more than a dozen sheepskins drummed at the same time. This small quantity may account for the absence of felting, as I am informed that where a large number of sheepskins are drummed together, felting invariably takes place.

IMPRESSIONS OF DUTCH WEST BORNEO.*

By Alexander T. Hough.

When five years ago I was drawing samples of "Tannadine" mangrove bark extract for Dr. Parker in the South Eastern wharves, under the eaves of that beautiful Gothic structure, Southwark Cathedral, I did not foresee the extraordinary cycle of events which has been responsible for my engagement in its manufacture.

Borneo, to the average individual conjures up visions of wild men, swamps and fevers. Swamps are plentiful, but one hears very rarely of fever in the Pontianak district, and the only wild men are the Dyaks, who generally keep to the interior, and have already become half civilized by contact with European pros-

* *Leather Trades' Year Book*, 1915 pp. 117–27.

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pectors, towards whom they are always friendly, provided such friendliness is reciprocated, otherwise they are a very dangerous enemy, even to trained, armed forces.

Pontianak is the principal town of Dutch West Borneo. There are about 220 Europeans here, and many thousands of Malays and Chinese. The commerce of the town is mainly affected through Singapore, Batavia and Soerabaya, about eight boats of 1,000 tons, more or less, assuring the service, the finest and most important being those of the Royal Dutch Steam Packet Company.

The industrial activity of the district is mainly directed towards coconuts, the exports amounting to about 100,000,000 per year. Besides this, large quantities are husked and the flesh is dried over smoke in a very crude fashion, some of the copra thus prepared being exported and the remainder rendered into oil by two local factories working with hydraulic pressure. The valuable coir and coconut milk are rejected as waste and would probably form a valuable source of exploitation.

The hide production is uninteresting commercially, about 20 animals being killed per week and the hides sent to Singapore. The writer has occasionally bought calfskins at 7d. each, a price which would make the European tanner's heart rejoice and arrest his proverbial grumble.

The nearest tanneries are run by the Chinese in Singapore, their staple tanning material being mangrove bark which, like all other catechol tanning materials when used alone, is quite unsuitable for producing leather resistant to wear and water. In Pontianak I have bought really smart shoes, locally made by Chinese, with good quality chrome, box calf, and glacé kid uppers, at 9/- per pair; but, the soles were of red Singapore leather and about 50 days wear finished them; although the uppers are still good for 6 months, repairs are useless as the red leather will not take the nails, besides which John Chinaman, is not ignorant of the dark mysteries of paper utilization. He is, in fact, an adept in the art, although I believe he has not yet been initiated into the uses of Epsom salts and sugar.

Mangrove bark is also widely used throughout Borneo and the Straits Settlements for dyeing "sarongs"—the native apology for a skirt—which the men and women wear without distinction;

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these are so convenient that many European women wear them also in the morning *en déshabillé;* the color scheme is generally gorgeous, and the patterns consist of flowers, birds, etc., wonderfully modified Scotch plaids also being very popular. Many of these sarongs, however, are German made.

Telok Ayer or Pulau Ayer, where is situated the factory of the Tannadine Company, Borneo, Limited is an island about 5 miles in circumference. Telok or Pulau means island, and Ayer means water in the Malay language, and the place derives its name from the fact that although several salt water tributaries meet around the island, yet there is always a very plentiful supply of fresh water, and in former times both Malays and Dyaks used to descend as far as here to replenish their supplies. It is 120 miles from Pontianak by river, the voyage occupying 12 hours on the company's steam launch. On arriving at the landing stage one sees the factory at the base of a hill, about 300 feet high, which encloses it in a complete semi-circle.

The entire male population is in the employ of the company and consists of 3 Europeans (manager, chemist, and engineer), about 70 Chinese, who work the factory and over 100 Malays, who are generally occupied in the swamps cutting mangrove bark. The climate is extremely salubrious and the district entirely free from fevers and epidemics. Delightful trips may be made into the jungle through the many paths made by the coolies, who cut firewood for the factory. Botanist and biologist alike may have a regal time; queer insects abound and many species of orchids may be had for the picking.

One is fairly safe without a gun or a knife as there is small chance of meeting any really dangerous animals in Dutch West Borneo. Occasionally one may happen upon an iguana, a boar, or a python, but they will make tracks upon seeing a human being approach. These wild folk are a nuisance around the bungalow; the boar will root up a whole garden of fruit and vegetables in a few nights, and iguanas and pythons have a peculiar taste for poultry. The python is easiest caught as he will swallow three or four hens, and find a corner to go to sleep to digest them, when he is easily despatched and skinned. The skin is pulled off like a stocking and entails no skilful flaying. The iguana skin, on the

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contrary is very difficult to remove, very strong nerve filaments holding it to the flesh, and it must be cut away inch by inch, and takes some 3-4 hours to flay one animal.

I have been very successful in curing these skins by liming 3-4 days, descaling and fleshing, deliming in acetic acid and tawing in strong basic alum solution made by adding a solution of sodium carbonate to a strong solution of alum until there is a slight permanent precipitate; the skins are completely tawed in 3-4 days and after sammying should be well staked. Crocodiles are fairly numerous, but I have only seen four and hooked one on a pork baited drag; this one I flayed with a Malay "Parang" (short sword) under the broiling sun, the thermometer indicating 44° C. He had evidently been busy as there were 4 pigs' hoofs, an entire cat and a native bracelet in his stomach, besides many bones.

There are many tanning plants in Borneo, but the majority are so sparsely scattered about that a profitable exploitation of them is impossible. The only really interesting uncultivated tree from a commercial point of view is the mangrove or "bacau," which lines the banks of the great Borneo rivers and whose gnarled roots are visible far above high water mark. The most interesting species are known locally as "Bacau'" and "Tengah"; the latter is slightly superior in tannin strength but is not used here, the Malays demanding half as much again for this bark as for "Bakau" because it will not strip, but has to be cut off the trees.

The Malay bark cutters live in large boats covered with palm leaf roofs and are towed to different parts of the company's extensive concessions by means of a steam launch. Having arrived at the place where they intend cutting, they pull their boats as far up the "parits" (small waterways), as possible in order to avoid the dangers of the open river; they then travel as much farther up as necessary in a very small canoe called a "sampan." Here they climb amongst the roots and undergrowth, select suitable trees, fell them with short axes and strip them of their valuable bark; this they carry to the sampan and make a series of trips down to the larger boat until it is full.

European supervision in this part of the work is quite impossible as it necessitates climbing among roots and all sorts of

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swamp growth, besides a certain habit of progressing in deep mud and slime. This, however, is not the worst; most of these Malays are very much scarred by sores caused by scratching mosquito and sand-fly bites, from which they protect themselves as much as possible by working in a smoky atmosphere. The sand-flies are much smaller than a pin's head and their bite is worse than that of a mosquito.

After 8-10 days the bark cutters will have collected about 3-4 tons of bark—sufficient to fill their boat—and will then stand out in the open river waiting for the steam launch to come along to tow them back. At the factory a Chinese clerk weighs the bark and rejects any bad stuff. If in collecting it has been left on the banks of the "parit," and covered with sea water at high tide and then left exposed to the sun, on breaking the bark the section will be black instead of a healthy red; tannin will have been destroyed and transformed by oxidation into phlobaphenes and the color will have been greatly increased. If again the boat has been stranded up a "parit" because the tides have not risen sufficiently to float it down, the packed bark, containing as it does 50 per cent. of moisture in the natural state, will heat and ferment with the development of penicillium glaucum, and a mucor, with the same results as described above. Bark which has been cut for over 12 days will show this defect more or less, and after 20 days becomes quite rotten and useless for extract making.

After being weighed in, the bark is carried into the factory, extracted, and the liquor at about 6° Baumé, is run into the vacuum pan for concentration, the extract produced being perfectly pure, untreated with chemicals of any description, mellow, and of good quality and strength; it contains more than 55 per cent. of tannin and shows about 11° red on the Lovibond tintometer. Its qualities are so well known that I need not describe them here.

There are certain difficulties one meets with in the analysis of tanning materials in the tropics. First, the solutions are always warm; I have rarely seen them indicate less than 30° C. and they are often as much as 33° C. This naturally produces a constant difference from analyses made in Europe. Then again, it is most important not to use a 10 per cent. stock chromium chloride solu-

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tion; a common and reasonable practice in England. If the chromium solution be not freshly prepared out here, it produces a non-absorbent hide-powder and consequently very high non-tannins extending over a range of 5 per cent. It is peculiar to remark that the hide-powder does not seem to suffer and may be kept intact for years without any special precautions.

In the warm and rather damp climate of the tropics, moulds very quickly develop on book-bindings, whether they are of leather or cloth, but more especially on the latter as the surface finish usually contains some sticky, organic matter, as starch, albumin, or gum, etc., which, when attacked renders the book very disreputable in appearance. This may be remedied by making a 1 per cent. solution of allyl isothiocyanate (artificial mustard oil) in methylated spirit and wiping over the bindings once a month with cotton wool soaked in this.

A certain amount of gambier is produced here by the Chinese, but it is dearer than in Singapore. Large quantities are used for chewing by the natives. The most beautiful women are those with the blackest teeth, and they contrive to blacken them by chewing a mixture of sireh leaves, (the betel pepper creeper) betel nut (areca nut) tobacco, cloves, gambier and slaked lime—quite a tannery; very few of the men chew this mixture.

As a race the Malays have very few virtues; they are not very intelligent, are incapable of speaking truthfully, lazy, improvident, unreliable, only work to satisfy their innate gambling instinct, are very sensitive to chicanery and credulous. They are generous, modest, and not great thieves when compared with the average Chinaman, who robs them on a large scale, and although they know it, they prefer to treat with a Chinaman rather than with a European. The Malay language is universal in the East Indies and is spoken by all its inhabitants, whether Javanese, Japanese, Hindoos, Chinese or Europeans. The language itself is a most nondescript mixture of nearly every other language, but is based mainly on Arabic as is also the caligraphy. It is said to be easy to speak, and it really is easy to pick up a few necessary phrases in a general sort of way, but a study of the language proves it to be as difficult as any European tongue, owing to the

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many shades of meaning of different words and the excessively large number of derived forms.

The credulity of the Malay is illustrated by the following anecdote:—A ganger came to me with the information that a dead relative had left a large and valuable stone for which he had paid £20. This he promised to bring for my examination with a view to selling it. A week or so afterwards he turned up with the stone. First he took from his belt a purse, from which he extracted a native-fashioned wooden case, which he carefully opened, exposing to view a perfect specimen of the glass ball used for closing certain lemonade bottles. He looked rather disgusted when I explained its use, cursed his forefather for a fool, and threw it into the river.

These people are too well protected by Dutch law. In Europe the usual impression is that these colored folk are the slaves of the white man; here however, the rôles are reversed; house servants who are paid from 30/- to 35/- per month and their rice, must be allowed to do practically as they wish and what they wish; no matter how well merited a reproach, they will leave without notice, and tell all the other servants your are bad people, and you are then the subject of a general boycott which is excessively inconvenient. These people will not engage themselves without monetary advances on their wages. In fact the best way to retain them is to advance them more than their monthly due, for a Malay will never leave an employer while in debt, and if he commences to repay his debt by large installments it is a sure sign that he wishes to get clear and leave.

This situation is partly created by the exigencies of the Dutch authority who tax the natives heavily and make them serve 40 days per year on road making, besides insisting upon their planting and harvesting rice to prevent famine, a decidedly wise precaution. They nevertheless, find the yoke too heavy and emigrate to British colonies where the authority is not so exigent, with the result that so much labor leaves the colony, that what remains can afford to be independent.

The average Chinaman is not so sensitive as the Malay and will take a large share of abuse without flinching. He is intelligent, thrifty and industrious, although when not working piece or

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in his own interests he will do as little as possible for his wages, and must be watched. He is a thief and a very wily fellow, inventive and a clever workman. His greatest vices are opium smoking and gambling, but the former is dying out.

The protection afforded Chinamen under British control is illustrated by the following story:—A Chinaman of Penang, having badly executed some task, was roundly abused by the English manager who afterwards struck the fellow with a slipper, a great insult to a Chinaman, who proceeded to complain to the police. Subsequently the English planter was summoned to appear in court, where he admitted the offence. The judge fined him $5 and the Chinaman left the court grinning over his revenge, whereupon the planter asked what a second offence would cost and the judge replied $10. A few minutes afterwards loud shrieks were heard proceeding from the court-yard, and when the police arrived, the same Chinaman was bleeding freely and rapidly developing two black eyes, with the planter standing over him ready to renew the attack. The latter was arrested and severely censured by the judge, who demanded on what provocation he had again beaten the Chinaman, whereupon the accused replied "Well your Honor I'd only one whack for $5 so I thought I'd have another go and take it out of him for $15, and please what will a third offence cost?" "What again" roared the judge, "Next time you will go to prison for contempt of court."

The mentality of the Straits born Chinaman is different in some respects from that of the man from China, and both regard one another with equal contempt.

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SOME NOTES ON LIMING.*

By Walter James and P. Ray Barker.

(In view of the fact, that it is often extremely difficult to reconcile "theory" with practice, it has occurred to the writers of the following article, that an attempt can be made to lessen this difficulty by encouraging the associate members—particularly the practical ones—to present their views upon any practical subjects. If this can be carried out successfully it should accomplish two things. On the one hand, the present practical and mainly passive associate members of the association will become more active, and more in direct touch with the purely scientific side; and, on the other hand, the scientific side will more readily see the requirements and the troubles and difficulties of the practical side.)

Various articles have appeared from time to time dealing with the merits and de-merits of various systems of liming. Some have even shown the loss of hide substance (estimated by Kjeldhahl's method) in various stages of the operation and from these figures have attempted to arrive at some basis for the formation of rules, to be observed under varying conditions. And yet no definite system can yet be presented which will give good results to all workers. Even when the chemical differences of various waters are known and errors rectified we still find that one worker swears by one method, and one by another.

When approached solely from the scientific side such things as actual time of hauling and method of setting, etc., are inclined to be overlooked, and it is noteworthy that much stress is laid upon these points by the practical workers. Dealing with sole leather liming where the obtaining of as large a pelt yield as possible is the main object, we find that this result is obtained in many ways, some of which appear somewhat opposed to scientific reasoning. A short sharp liming has always been considered correct but how often does one hear the practical man say "Give them time." The following illustration of some practical liming will explain what we mean.

Hides in packs of 20 were limed in small pits situated inside the building with a capacity of about 450-500 gallons. The system was as follows: The hides were thoroughly soaked in water and placed in lime which had previously received one pack. On

* *Collegium*, London Edition, May, 1915, pp. 136-7.

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the second day these were hauled, and on the third day a new lime was made in the same pit. The goods were again hauled on the fourth day, and every subsequent day, until date of unhairing. At the end of 8-10 days these hides were unhaired quite easily.

Further packs of 50-60 hides were limed in a similar manner to the above in larger pits of approximately 1,500 gallons in the open. The proportion of lime used as well as volume of water was similar in the two cases. The hides outside, in the larger pits required 14-16 days and even so long as 18 days to complete the liming. These hides were better limed and much plumper, although the time was much longer. Further, it was found that by allowing the hides to remain in the inside limes a few days longer a gain in weight was obtained. Beyond the fact that the temperature of the inside limes would be greater than the outside, all the other factors were equal. The higher temperature inside quickened the unhairing, and, although the liming was short and sharp plumpness was not obtained. This may be accounted for by the lowered solubility of the lime as well as the slight falling, due to temperature, but in any case it certainly represents one of those cases where short liming was not an advantage.

In the above system of liming the hides will not unhair out of the old lime; but after the second day in the new lime some slipping of the hair is noticeable. Sometimes this is even observed after the first day, the cleanliness and general condition of the hide influencing the actual time required. The first effect of the new lime is to plump. After this the hides gradually fall while the hair is being loosened. Subsequently in the same lime, without further addition of CaO plumping takes place and this appears to reach a maximum for that lime at a certain date—a date which is ascertained by practice. With this system of liming it is possible to obtain very high yields of pelt to green, but care must be taken to unhair at the proper time—not too soon—nor too late.

There is one other aspect of liming which I should like to present. In the ordinary way it is usually acknowledged that for dressing leather longer liming is desirable than for sole. This may

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be the result of a general consensus of opinion upon the matter. That it is not necessary is borne out by some work which we have carried out. Hides were sole-leather limed resulting in 95-100 per cent. pelt yield, and afterwards delimed and puered before tanning. The pulling down action was only allowed to take place in the puer, and not in the limes. The general result is a much fuller leather with well filled flanks. Hides which have been limed for some time—with some pulling down action—invariably show thinner flanks. In fact one wonders whether all classes of leather, hides and skins do not require a definite maximum amount of liming to produce the best results for all purposes; and whether the pulling down action to suit the various kinds of leather is not best obtained in subsequent operations.

The writers invite criticism or further views upon this subject and particularly address this to the practical associate members of the Association.

SOME NOTES ON LIMING.—AN ANSWER.*

By Hugh Garner Bennett, M.Sc.

In the *Collegium* 1915, p. 136, Messrs. James and Barker present some of their difficulties in reconciling "theory" and "practice." The frank discussion of such difficulties would do much in many cases to clear them away completely, and it would seem perhaps that the *Collegium* could in this way fulfil a useful and valuable function. Inasmuch as in this case criticism is invited, the writer ventures very cordially to offer it.

Firstly.—One of their difficulties is the time which it is desirable to take for liming sole leather. They find this can be done in "ways, some of which appear somewhat opposed to scientific reasoning." "Theory" is said to indicate a short liming, whilst "practice" says "Give them time." Both these standpoints clearly need more definition and explanation. Does "practice" say "in all cases of hides for sole leather make the liming as long as possible"? Does "theory" say, without qualification, "get the hides out of limes as soon as possible"? Is there, in reality, any such opposition as this between theory and practice? There is

* *Collegium*, London edition, Aug. issue, pp. 213-15.

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something radically wrong both with the theory and the practice that indicate such courses as these. The writer finds it *utterly impossible to imagine any system of liming in which theory would say "less time," and practice "more time."* If Messrs. James and Barker have apparently found such circumstances, they may be quite certain that there is something seriously amiss with either their theory or their practice, or with both. There is something essentially at fault in a theory that overlooks points upon which the practical workers lay stress. To ignore such things as hauling and setting is not a scientific attitude. *It is extremely unscientific to overlook points which are not chemical.* There is something equally wrong with the practice of liming which ignores everything but the yield of pelt. Practice which wastes hair and hide substance is not worthy of much defence.

Secondly.—The supposed inconsistency of theory and practice is very frequently due to the vague and ambiguous manner in which many so-called "practical men" state their case. An example may be taken from the paper under discussion. "The hides . . . required . . . 18 days to complete the liming. These hides were better limed and much plumper." What do the authors mean by "required" and what by "better limed"? When, according to Messrs. James and Barker, is a hide limed? Do they mean ready to unhair, or do they mean fully plumped? From the methods actually described it is clear that they consider the process finished when the goods are ready to unhair, and they then judge the method by the yield of pelt. A hide is "limed" when ready to unhair and "better limed" if it gives a better yield of pelt when ready to unhair.

Now the writer suggests that the standpoint should be reversed. He would start from the assumption that the maximum yield of pelt must be obtained, and that the problem is to adjust the method until the goods are just ready to unhair on the day they are fully plumped. This "theory" says a hide is "limed" when fully plumped and just fit to unhair; also, that if ready to unhair before being plumped or *vice versa* there is something radically wrong with the process. From this point of view Messrs. James and Barker's longer process certainly seems the better of the two, but the conclusion to be drawn is not that longer processes are

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better, but that *a longer process is better when the shorter process is a thoroughly bad one.*

Thirdly.—Another ambiguity needs to be cleared up. What do Messrs. James and Barker mean by a "sharp" liming? Sometimes they use it apparently to mean "quick," implying merely a shorter time and a more rapid process. Sometimes they use it apparently to mean "caustic" implying that the limes were fresher, less impure, *i. e.*, less nitrogenous matter and bacteria present. It should be mentioned that the latter is the usual significance, even with practical men, who generally use the word "mellow" as its opposite. The mischief of such "practical" terms is just this tendency to mean anything in turn according to circumstances. Now if the latter (and usual) interpretation of "sharp" be accepted by Messrs. James and Barker, they certainly should not apply it to their shorter process. That process cannot possibly be described as a "sharp" process. This is clearly shown by two facts:—

1. The goods unhaired usually, and quite easily, several days before they were fully plumped.
2. The goods were unhaired out of a lime liquor which was a week old, or more.

Their statement that "although the liming was short and sharp, plumpness was not obtained,"—contains a pretty alliteration, but is not in accord with facts.

Fourthly.—Messrs. James and Barker state that if "as large a pelt yield as possible is the main object," then "theory" favors a short liming. The writer has never heard of such a theory, which is surely absurd on the face of it. Who has proposed the theory that a short time in limes means a better plumped hide and a better yield of pelt?

Theory *has* an argument for shortening the time of liming, but that argument is not plumpness of pelt. Theory looks a little further than the limeyard and considers the possibility of a greater yield of leather as well as of pelt. Theory indicates that the longer the hides remain in lime liquors the more hide substance is dissolved. The theory of sole leather manufacture also indicates that the less hide substance dissolved the better for weight and for quality. Theory therefore says that *if hides are*

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fully plumped and just ready to unhair, the shorter the time in limes the better, as hide substance is saved. If, on the other hand, hides are *not* fully plumped, theory would propose not a shorter liming but a sharper (more caustic) liming. Practice, however, would propose a longer liming because it knows no other way of plumping! Theory points out several other ways of obtaining plumpness which are better than longer time.

The fact is that Messrs. James and Barker have not tried a short sharp liming. Their outside process is not short, and their inside process is not sharp. Neither process indeed is very short or very sharp. Both processes need shortening, and sharpening, but the inside process especially needs sharpening, and the outside process especially needs shortening.

The changes needed are fairly obvious to modern theory:—

(*a*) Sharpen both processes by finishing out of a fresher lime.

(*b*) Sharpen the inside process further by the use of caustic soda, or carbonate of soda.

(*c*) Shorten and sharpen the outside process by the use of sulphide of soda.

With these modifications Messrs. James and Barker will find that the maximum amount of hair, of pelt, and of leather will be obtained simultaneously and "theory" will be strikingly confirmed by "practice."

Fifthly.—The writer would like to point out to some scientific members that some of the actual facts recorded by Messrs. James and Barker are a very interesting contribution to leather chemistry, and call for theoretic attention. They find that the plumpness of hides in limes attains successive maxima. What is the cause of the fall in plumpness and of the subsequent rise for the second time? It would be of great interest if other workers could confirm these facts. The writer ventures to suggest that the fall in plumpness is due to an increasing proportion of causticity due to ammonia, and that the subsequent rise in plumpness is due to the escape of ammonia into the air, owing to the hauling and setting of the goods.

The question of the comparative time of liming for sole and dressing leathers, the writer will leave to some other critic.

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ANALYSIS OF TANNING MATERIALS.*

Reply to Dr. Callan.

By H. Garner Bennett, M.Sc.

In *J. S. C. I.*, 1915, p. 646 (see this J., Aug., 1915, p. 428) some criticism is offered by Dr. Callan as to the detannization effected in the method of tannin analysis recently suggested by the writer (*J. S. C. I.*, 1914, p. 1182; this J., Feb., 1915, p. 87).

In testing for complete detannization Callan uses the metaphosphoric, salt and gelatin test devised by Stiasny, and states that this "will not show 150 milligrams of gallic acid in 50 cc., which is about the maximum amount of gallic acid likely to be present in a detannized solution even after concentrating to half its volume." Both points involved in this statement may be seriously questioned.

1. The writer finds that a 0.3 per cent. solution of gallic acid (*i. e.*, 150 milligrams for 50 cc.) gives a distinct turbidity with Stiasny's test, indicating the apparent presence of tannin. A solution of gallic acid any stronger than this, *e. g.*, a 0.5 per cent. solution, will give a very decidedly positive result with Stiasny's test, which is useless therefore for distinguishing tannin from gallic acid in such solutions. Indeed, Stiasny himself has, in correspondence with the writer, repudiated his own test as "unreliable in the presence of gallic acid." Further, tests with solutions of catechin (the typical non-tannin of the catechol tans) have shown that Stiasny's test is even more unreliable in the presence of catechin than in the presence of gallic acid, decidedly positive results being obtained in solutions containing less than 0.3 per cent. catechin.

2. It is by no means certain that the gallic acid (or catechin) in non-tan filtrates never exceeds 0.3 per cent. In the present official method of analysis the total non-tannins are such as frequently to exceed this, especially in the cases of babla, lentisco, and gambier; and in the first and last of these the proportion of gallic acid and catechin respectively of the total non-tannins is known to be very large, and may easily exceed 0.3 per cent. in the non-tan filtrates. Further, in the author's method of analysis, although the dilution is greater, the proportion of non-tans absorbed

* *J. S. C. I.*, Aug. 16, 1915, p. 822.

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by the hide powder is also much less, so that in this case also the percentage of astringent non-tans may easily reach the point at which positive results are obtained with Stiasny's test. In the author's method the non-tannins estimated are often more than double the amount estimated in the present official method. Again, if these non-tan filtrates are to be concentrated to half their volume before the test is applied, there is no doubt whatever that 0.3 per cent. solutions of gallic acid and of catechin will be obtained with many materials.

3. It seems to the writer that the official test for detannization with a 1 per cent. gelatin 10 per cent. salt solution is sufficiently delicate for its purpose. It will detect one part in 100,000 parts water of gallotannic acid, which tannin is fairly typical of the commercially important pyrogallol group. Even with the extra dilution proposed by the writer this test involves a maximum error of about 0.1 per cent. An error of this order is negligible compared with the errors of up to 12.0 per cent. which are avoided by the author's method of analysis. Well may Dr. Callan conclude concerning this method that "in all probability the gain in accuracy owing to the reduced absorption of non-tans is more than the error introduced by the non-absorption of traces of tannin." This is particularly true when the latter error has not yet been demonstrated. When errors of up to 12.0 per cent. can be shown with a maximum experimental error of 0.1 per cent., the search for a more stringent test for tan seems to border upon the absurd. All the tests for tan yet devised, more delicate than the gelatin-salt test, have been found to give a positive result also with the astringent non-tans, which fact condemns them in testing for complete detannization.

4. In the same paper Callan records experiments with the author's method and German hide powder. It seems futile to combine a method devised to reduce the absorption of non-tans, with a hide powder calculated to increase such absorption. The strong affinity of German hide powder for non-tannins has been so often proved and is so generally known, that its use with any method of analysis is now thoroughly discredited.

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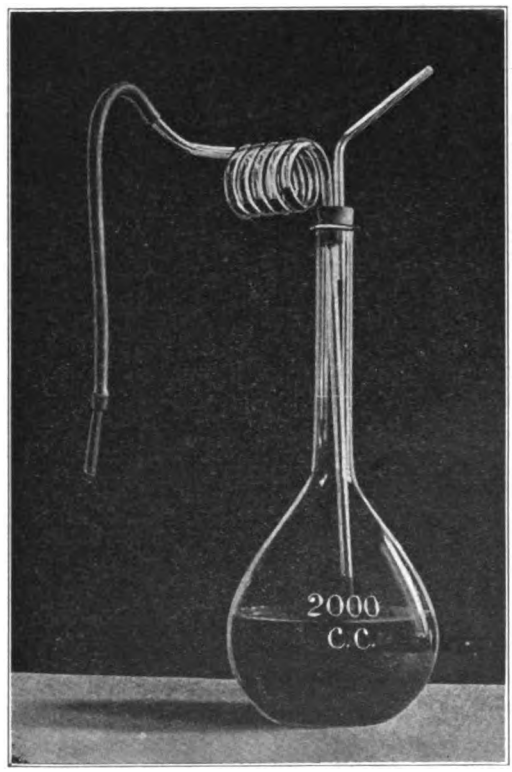
DEVICE FOR EMPTYING FILTERS.

By J. Earle McNutt.

After trying various devices for removing tanning liquors from the filter paper in the preliminary filtration for soluble solids, we hit upon the device shown in the accompanying cut.



The siphon as used in this laboratory, is composed of a two liter flask with a long neck, to accommodate the long stem of the siphon, which is made of 8 millimeter glass tubing, and is 14½ inches long to the center of the coil. The coils are five in number, 2 inches outside diameter. The projection beyond the coils is about 6 inches long. To this projection is attached a 10-inch

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piece of black rubber tube fitted with a hard rubber nozzle. We have tried a glass nozzle, but find that it is almost impossible to see it in the liquor, thus increasing the danger of piercing the bottom of the filter. An air vent made from a piece of 8 millimeter glass tubing about 8 inches long and bent in the middle to about 45°, is placed in the rubber stopper supporting the siphon in the flask.

To operate, place the nozzle of the siphon in the liquor and draw gently on the air vent until the coils and stem are filled. After this the liquor will flow freely from the filter into the flask. When the liquor is removed from the first filter, pinch the tubing back of the nozzle and place it in the next filter. On releasing the tube, the siphon will start to flow again. The liquor can be removed to the last drop.

The principal use of the coil is to retain the column of liquor, thus minimizing the chance of losing the siphon, when the air enters the nozzle. It is safe to let the liquor flow through the siphon until small air bubbles show back of the rubber tubing.

In making the siphon, do not use over five coils. More than this number of coils will hold enough liquor to counterbalance the weight of the liquor in the stem, making it necessary to hold the flask below the work table; otherwise, the flask can rest on the table during the removal of the liquor. We find that with a siphon of the above dimensions we can remove liquor from twenty-five filters in from four to five minutes.

ELK TANNING CO. LABORATORY,
Ridgway, Pa.

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JOURNAL OF THE ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS.

The close relations which formerly existed between leather chemists and the Association of Official Agricultural Chemists will for readers of the JOURNAL give more than ordinary interest to the announcement that the Association with which leather chemists were formerly affiliated, and in which a number of our members are still active, is hereafter to publish a journal. The first number of the new journal has been issued under date of May 15, 1915. It is published by the Williams & Wilkins Co. Baltimore, Md., for the Association. It is to appear quarterly, the price being $5 a year. The first number contains 168 pages. The pages are 7 by 10½ inches in size, half an inch larger each way than this page. The type is 10 point, the same size as this, and the lines are ½ inch longer than these, with three more to the page. It is handsomely printed on a good grade of unglazed paper, and is sewed together, not wire-fastened. The cover is light tan in color, and the arrangement of title, etc., conservative, tasteful and dignified. The manner in which the tables, formulas and other special matter are set up shows skill and experience on the part of the printers, and altogether the new journal is a most creditable piece of bookmaking.

The matter of the first number consists of a part of the proceedings of the thirtieth annual convention of the Association, held at Washington, Nov. 17th to 19th, 1913, preceded by the Constitution and By-Laws of the Association. A list of nearly 300 members and visitors present is given. The papers are as follows:

Report on Phosphoric Acid, by A. J. Patten and L. S. Walker.
Report on Nitrogen, by C. L. Hare.
Report on Determination of Potash, by H. B. McDonnell.
Report on Availability of Potash, by E. E. Vanatta.
Determination of the Availability of Potash in Feldspathic Fertilizers by Means of Pot Experiments, by M. F. Miller and E. E. Vanatta.
The Perchlorate and Gravimetric Cobalti-nitrite Methods for the Determination of Potash, by T. D. Jarrell.
Report on Soils, by G. S. Fraps.
Differences in Lime Requirements as Indicated by the Veitch Method, by A. W. Blair and H. C. McLean.

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Method for Determining the Lime Requirement of Soils, by C. H. Jones.
The Effect of the Presence of Ammonium Carbonate upon Humus Determinations, by W. H. McIntire and J. I. Hardy.
Humus Determination, by O. C. Smith.
Report on Nitrogenous Compounds in Soils, by J. K. Plummer.
Report on Inorganic Plant Constituents, by W. H. McIntire and B. E. Curry.
Report on Insecticides, by S. D. Averitt.
A Comparison of the Iodine Titration and Zinc Chloride Methods for the Analysis of Lime-Sulphur Solutions, by R. C. Roark.
A Short Method for the Analysis of a Lime-Sulphur Solution, by S. D. Averitt.
Report on Water, by W. W. Skinner.
Report of Committee A on Recommendations of Referees, by B. B. Ross.
Report of Committee on Availability of Phosphoric Acid in Basic Slag, by C. B. Williams.
Report of Committee on Food Standards, by William Frear.
Report of Committee on Editing Methods of Analysis, by J. K. Haywood.
Report of Committee on Practicability of Organizing for Study of Vegetable Proteins, by L. L. VanSlyke.
Report on Food Adulteration, by Julius Hortvet.
Report on Colors, by W. E. Mathewson.
Report on Fruit Products, by H. C. Gore.
Report on Wine, by B. G. Hartmann.
Report on Beer, by J. G. Riley.
Report on Distilled Liquors, by A. B. Adams.
Report on Vinegar, by E. H. Goodnow.
Report on Flavoring Extracts, by A. E. Paul.
The Direct Determination of Volatile Oil of Cloves by Distillation with Steam, by Julius Hortvet.
President's Address, by G. S. Fraps.

The report of the Committee on Colors embraces a study of colored imitation liquors by a number of collaborators, to determine the colors used. The method most used is based on the relative solubilities of artificial coloring matters in various immiscible solvents. An extended study of more than a hundred coloring matters with respect to their solubility in fifteen solvents is given in tabular form.

The report and discussion on lime—sulphur solutions contains much matter which ought to be studied in connection with the work on beam-house problems.

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The Presidential address touches on various matters of general interest to chemists, and no apology is needed for presenting extensive quotations from it:

Agricultural chemistry is so closely interwoven with the other sciences which have been applied to agriculture, that it is practically impossible to disentangle them. Hence to a certain extent the progress of the chemistry of agriculture is closely related to the progress of other agricultural sciences and to agricultural science in general. The contributions of the chemist to agricultural science have been so many, so varied and so important that for a long time the sciences applied to agriculture have been termed "agricultural chemistry." This period is passing, and the term "agricultural chemistry" is being more restricted in its significance, but the field is still broad, and the harvest bountiful. * * *

There has been a tendency in some colleges to discontinue the teaching of agricultural chemistry and to divide the subject matter between the agronomist and the animal husbandman. It is a serious question whether such tendency is in accord with the known laws of specialization in science. There is no doubt that as time goes on the agricultural chemist must specialize more and more in one of these fields of work, but there is a difference between the specialization of the scientist in his own field and the attempt of other branches of agricultural science to take over the work of the chemist, or of the chemist to take over other branches of agricultural science. As I see it, both the agronomist and the animal husbandman have their special problems. They must have their special training in their own fields, and while this training must include some chemistry, it is not sufficient in quantity to make them into chemists. On the other hand, the chemist must first of all be a chemist. The agricultural chemist must have knowledge of soils and nutrition, but he should have predominant chemical training and chemical methods of thought. The agronomist and the animal husbandman undoubtedly need the aid of the chemist in the solution of their problems, but they should not seek at one and the same time to be both agronomist and chemist. The result of such an effort is either an agronomical chemist or a chemical agronomist. It often results in the chemist becoming also the agronomist. What agricultural science needs is the highly trained agronomist, working, where needs be, in co-operation with a highly trained chemist, who has perhaps specialized in soils and fertilizer chemistry, each assisting and aiding the other. The same is true of the animal husbandman. We need the animal husbandman, highly trained in his field and with a full knowledge of its peculiar problems; working in co-operation with the agricultural chemist, highly specialized in the chemistry of nutrition. In this way, we shall avoid those errors which we so often see when a man enters into a field outside of his special training, errors which the specialist immediately recognizes. * * *

These matters will adjust themselves in time. We need not fear that the science of agriculture will ever be without the need of agricultural

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chemists. Our ranks have not thinned, but each step of progress has rather added to our numbers. The Adams Act, of March 16, 1906, for example, which is one of the most important events in the recent history of agricultural science, has increased the number of agricultural chemists, as well as of other agricultural investigators. The act is important, not only because it increased the number of scientific agricultural workers in the experiment stations and their facilities for investigation, but because it affords to the experiment stations opportunity for fundamental research work. The passage of the Adams Act indeed marked an epoch in the history of agricultural science. The experiment stations had previously done much valuable work, and accumulated much data, a fact which the passage of the Adams Act itself recognizes, but they had such large demands upon them for immediate and practical information that they had little time for the investigation of fundamental things, which are no less practical in their final application, but require more time and patience, and are less obvious in their practical applications. * * *

Striking progress has been made in recent years in the survey and mapping of soils. In this work the Bureau of Soils is easily the leader. There is a tendency in some quarters to regard the survey, mapping and analysis of soils as an end in itself. It is true that such work is highly important, but it should also be regarded as a basis on which to make further soil investigation, so that we may become fully familiar with the properties and characteristics of each type. In a sense, the soil survey should be regarded as the beginning of soil studies. In other respects our knowledge of soils has been increased by recent investigations. We now know more concerning the nature and constituents of the organic matter of the soil, and something more concerning its biological properties. We also know that, on an average, the needs of a soil for fertilizer nitrogen in pot experiments is related to the total nitrogen of the soil. We know that the active potash of the soil is related to the average needs of the soil for potash in pot experiments, and that plants have the power to exhaust the active potash, and to take up more potash than they need. We know that, on an average, the active phosphoric acid of the soil is related to the needs of the soil for phosphoric acid in pot experiments. The relation of pot experiments and the analysis to field needs must be worked out. * * *

In the field of animal chemistry, decided progress has been made in recent years. We must now recognize the possibility that, in digestion, proteins of different kinds may be split up into different products, some of which may be unfit for use as structural material in building up animal proteins, and so must be discarded. We know that this is possible, but we have not yet secured positive evidence that such a thing occurs with any of the various proteins fed to domestic animals. Such studies may be expected in the future. It has been shown that the digested materials of different feeds have different value to the animals. One pound of digestible nitrogen-free extract in corn has a much greater value than one

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pound of digestible nitrogen-free extract in straw. The fact that there is a difference in the value of the digested nutrients of the same class but from different feeds has been clearly shown by the work of Kellner and of Armsby. It is a step forward to recognize the differences in the value of digested nutrients, and to adjust our tables, our rations and our calculations accordingly. There is abundant room for work along this line, but enough has been done already to justify this advance. Nearly every American book which deals with the feeding of animals still assumes that the digestible nutrients of one feed are equal in nutritive value, pound for pound, to the digestible nutrients of the same class in other feeds. These books must be rewritten. * * *

Our facilities for scientific investigation have been increased by the Adams Act. Our supervision over foods, drugs and feeds has been enlarged and rendered effective through the Federal Food and Drugs Act. We have made great progress in the survey and mapping of soils, and in our knowledge of their properties and chemical composition. The science of animal nutrition has made such advances as to render it necessary to revise almost all books dealing with the subject and to modify our methods of stating the nutritive values of feeds and our methods of calculating rations for feeding animals. These have been the four chief lines of advance of agricultural chemistry in recent years.

ABSTRACTS.

Chemistry and Analysis of Fats for 1914. W. FAHRION. *Zeit. angew Chem.*, 1914, Aufsatzteil, 161-70, 183-92. The war has greatly affected fat industries; crude materials are dear; recovery of fat from sewage waste has greatly developed. K. Kropat in determining fat in butter and cheese by the method of Gottlieb Röse, adds tragacanth to effect better separation of the layers. For the technical extraction of fats, A. Kosel prefers benzin, b. p. 80-105°; benzol separates with difficulty from water. "Tri" attacks iron less than "tetra" but is dearer than benzin. Oil cake retains ½ to 1 per cent. fat compound with 6-10 per cent. by pressing. W. Blow determines small amounts of fat in textiles, blood, etc., by extraction with alcohol-ether, and mixing the extract with water; the turbidity is compared with that from a standard fat solution. According to A. Bömer, the difference in melting points between glyceride and free acid is constant in swine fat. Likewise mixtures of swine fat with cocoanut, peanut, sesamé and cottonseed oils, 5 per cent. of tallow can be detected by this method. Hardened fats lower the difference in melting point still more than tallow and the phytosterin acetate test must be used. Sprinkmeyer and Diedrichs use the mother liquors of the two first glyceride crystallizations for the acetate test. Various authorities find that the discrepancies in viscometric tests are greater than the attainable accuracy. Raffo and Adanti find that free acids give more marked differences than glycerides and enable the detection of foreign oils. W. Arnold recommends to

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determine refractive indices of all oils at 40°; it was found that these decreased with increased saponifiable number for equal iodine number. C. Ellis showed that on hydridizing fats the index sinks and increases on oxidation. A. A. Besson uses ether instead of petroleum ether for the extraction of fatty acids, and weighs the free acid after drying in the extraction flask heated in a nickel dish over the water bath. Facchini and Dorta separate saturated and unsaturated acids by dissolving 10 grams acid in 90 cc. acetone, adding at boiling temperature 10 cc. aqueous alkali (strength unspecified); on cooling the K salts of saturated acids separate, are pumped dry and washed with acetone. Arachidic acid may also be separated from stearic and palmitic acid by fractional precipitation. Weiser and Donath recommend the determination of iodine number by the $KBrO_3$ method, using 50 per cent. excess Br, time ½-4 hours. A. Gemmell finds on brominating fatty acids in etherial solution that the precipitation with vegetable oils were not pure hexabromides nor pure octobromides with animal oils. Neither was there any relation between iodine and hexabromide numbers. Marcusson and Böttger obtained from various fish oils 10-34 per cent. octobromclupanodonic acid, diffusing solution in benzol; this can be reduced by zinc and gluco-acetic acid to the free clupanodonic acid. (This acid, $C_{18}H_{28}O_2$, the J. D. Riedel Co. declares to be not a single substance.) Fish oils which have been heated until odorless no longer give octobromides. Fish oils are proven in neats-foot oil when the yield of octobromide exceeds 1 per cent. and the inner iodine number is above 90. (Fahrion remarks the yield is higher with more concentrated etherial solutions of the fatty acid, say 10 per cent.) H. Thaysen proposes 2 per cent. as maximum unsaponifiable in colorless cod-liver oil, 3 per cent. in yellow and brown oils. J. Marcusson and G. Meyerheim state that the stearin constitutes 33-35 per cent. of the unsaponifiable in vegetable oils, and 8-14 per cent. in animal fats. The iodine number of the stearin-free portion is 56-78, about the same as for stearin itself, hence mineral oils can generally be determined in this way. Aniline dyes may be added to mineral oils to mask the reaction for rosin oil (Storch-Morawski), hence these should first be extracted with HCl until it no longer reddens. The fat hardening (hydridizing) industry has developed; 24 plants (including 6 in America) are listed. A. E. Sandelin reports the saponifiable number (192.7) of whale oil is lowered to 83.7 and the refraction number (at 40°) from 64.1 to 48.9. The principal consumption of hardened fats so far is in soap-making; oil works Germania furnishes 10 per cent. of total fat used for German soaps. There is now less complaint on the score of lack in foaming power. W. Herbig has studied Turkey red oil, neutralizing the free acid and dissolving neutral fat in acetone. The acid number of the fatty acids in the neutral fat was 134-140 and of those from the salt 155-160; the ratio between acetone extract and fatty acid was for Monopol soap 1.13, Turkon oil 1.45, and ordinary Turkey red oil 1.78; Monopol soap gives up its fixed sulphuric quantitatively on boiling with HCl. Several authorities advocate the Hehner method (modified) for glycerol determination. Bosshard and

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Huggenberg have studied the determination of free alkali in soap and find several sources of error; alkali carbonate is not entirely insoluble in alcohol, especially when much H_2O is present in original soap; alkali is retained by all filters; dissociation of soap is not entirely prevented by salting out. They propose to dissolve the soap in 50 per cent. alcohol precipitate cold with $BaCl_2$ and titrate free alkali with N/4 stearic acid (alcohol solution), naphthol-phthalein indicator. P. Heermann finds above method too roundabout for practical work and giving only 90 per cent. of the free alkali. W. J. K.

The Preparation of Tanning Liquors. G. GRASSER. *Gerber*, 1915 [41], 101-2, 117-18. Two methods of extraction are in vogue: (1) in open pits, (2) in closed batteries. The first, dug in the ground, may be lined with tarred wood, but in modern practice are often constructed of cement, the walls being built up of tile and then coated with cement. The number of pits can be 4-20 or more, according to need, best arranged in two series. The walls before use should be tarred or coated with water glass to prevent action of the liquor on the lime of the cement, especially if Neradol D is used. The vessels used in the closed batteries are of copper and this system has the advantages of economy in heat, less waste through oxidation and substitution of steam pressure for pumping the liquors. The fundamental rule in extraction is the supply of fresh, hot water to the nearly exhausted material and the transfer of the successive liquors of increasing strength to materials which are also progressively stronger in tans. The frequent practice of treating exhausted material with used liquors from the fore-tannage is to be rejected as worthless. Such liquors normally contain but little tannin and are loaded with non-tans which render them unsuited to dissolve out the residual tannin in the almost spent material. Oftener, besides this, the old liquors contain lime which precipitate tannin or annul its tanning power if in solution. The use of hot water instead is rational since the residual tans are only soluble hot, although an excessive heat on extraction of the fresh material would have decomposed some tan-stuff and lowered the rendement as shown by Procter and Parker's researches. Eitner has shown that high pressure extraction also decomposes tans. Nevertheless heat is the best agent for circulation of the liquors and obviating their darkening through oxidation when pumped. Also pumped liquors are turbid, requiring more clarifying. For filtering turbid liquors, fresh material should be used and never spent bark, etc., which give up water to the liquor and abstract concentrated tannin, requiring another extraction to prevent loss. W. J. K.

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A STUDY OF THE CHANGES IN SKINS DURING THEIR CONVERSION INTO LEATHER.

A thesis submitted in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the University of Michigan.

By Anton Augustus Schlichte.

ACKNOWLEDGEMENT.

The generosity of Mr. Carl E. Schmidt in establishing a fellowship in tanning at the University of Michigan, has enabled the author to pursue for 3 years, the studies outlined in this thesis. Mr. Schmidt has, moreover, given freely of his time and experience and it is a pleasure at this time to express appreciation, not only for the financial assistance rendered but more especially for the able counsel so unstintedly afforded.

Acknowledgement is also due Mr. V. A. Wallin for his interest and courtesy in making possible the completion of the experiments on heavy leathers.

The author wishes to thank sincerely, Prof. A. H. White for his constant interest and hearty co-operation during the entire time consumed by this research.

INTRODUCTION.

The use of hides both as skins and leather for protection against cold and rain, for weapons, or for ornaments, dates back to the remotest history of man.

While the hides were tanned in the earlier times with the hair on, methods were soon found to remove it and thus improve the product. The first substance used was probably wood ashes and this continued as the standard for some time. After tanneries were established, for up to this time the tanning was done only on a small scale, new substances were sought for, and lime, one of the oldest depilatory agents, was used. The method followed was to slack the lime in pits and soak the hides in a saturated solution of calcium hydroxide. This method although slightly modified has remained practically the same for centuries.

The tanning process was and is in general the following:

1. Hides are soaked to remove blood and dirt and to bring them back as nearly as possible to their original condition.

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2. They are placed in pits containing milk of lime, bacteria being always present and sulphides being frequently added, for from 3 to 18 days until the hair "slips" easily, that is, can be easily removed.

3. They are then bated to remove lime and bring the skin into the desired physical condition. The bate may be either acid or bacterial.

4. The next step is the pickling process in which the skins are treated usually with salt and sulphuric acid.

5. Then follows the tanning process proper, which may be either a mineral or a vegetable tannage.

6. The last step is a finishing process.

The entire tanning process has thus far been outlined to show the dependence of the finished product upon the correct performance of each succeeding step of the process. It is only through tests on the finished leather that the effect of any alteration in any step of the process can be detected.

The liming process is the one studied in greatest detail in this paper but any changes due to this operation can be detected only in the finished product. Moreover, the method of soaking must, because of its influence, also be specified. The object of soaking hides is to cause them to resume as nearly as possible their original clean and pliable condition. This part of the process while not so important when green hides are used becomes a matter of great importance when dried hides are to be investigated. The length of soaking, number of changes of water and the acids or alkalies which may have been added, all have an effect on the final product. Should the hides be soaked too long or should the water not be renewed frequently enough, bacteria multiply and a part or, in extreme cases, all of the hide may be lost. On the other hand acids and alkalies cause swelling of the hide and if too much of either be added the hide will be "plumped" too much.[1] This, while not fatal to a good final product, has disadvantages and as a rule causes trouble.

The object of liming is not alone the removal of the hair but also the loosening of the fiber bundles. More surface is thus exposed and hence the tanning agents are taken up more readily.

[1] Jettmar Handbuch, p. 56.

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In the vegetable tannage this makes a heavier leather. In the mineral tannage the loosening of the fiber bundles makes a more pliable leather.[2] The latter object is of great importance in the chrome tannage which is the method most used in manufacturing light or upper leathers. The hides after soaking are placed in pits in which an excess of calcium hydroxide is always present and to which some sodium or arsenic sulphide may or may not have been added. The hides are "hauled," that is, taken out and the lime "bettered" once a day until the hair "slips" easily. It requires much practice and experience before one is able to tell exactly whether a hide is done or not, and the method is not only unsatisfactory but also very unscientific, for the personal equation of the operator plays too important a part. The hides are then soaked in warm water, paddled and beamed. In the latter process the skin is placed over a piece of wood semi-circular in cross section and the hair is removed with a blunt knife. The long hairs comes off very easily but the fine or "ground" hair and the pigment, especially in the case of black skins, cause some trouble. Part of the intercellular substance, corium, "scud" or "gneiss" and some lime soaps[3] are also removed in the treatment

The next operation, "bating," has as its main object complete removal of the lime remaining from the previous treatment. The loosening of the fiber bundles, however, is also materially aided by bating and this, as before mentioned, is, in the case of light leather, of greatest importance. The bates most commonly used owe their activity to bacteria and are frequently more or less unsatisfactory and harmful to the skins. Bates of known bacterial cultures are used somewhat and give good results, but the most common ones consist of organic acids such as butyric, lactic, etc.

The skins are then pickled. The pickling consists usually of a treatment with sulphuric acid and salt. Pickling reduces partially the excessive swelling caused by an acid bate. Another object without doubt, is to furnish some free sulphuric acid which is considered necessary in the subsequent chrome bath. This sulphuric acid is probably absorbed by the skin and thus carried over to the tan bath. This finishes the treatment received by the

[2] *Gerber*, No. 938, p. 253; Procter's Principles of Leather Manufacturing, p. 126.

[3] Procter's Principles of Leather Manufacture, p. 136.

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skins in the "Beam House," which covers a highly important division of the tanning process. The most important part of the beam house work is the liming process, and hence this was made the object of the subsequent investigations. The object was to gain some insight if possible, into this apparently simple but actually very complicated process and furnish something of practical value to the industry.

It seemed obvious that some accurate way of controlling the liming and of judging the product afterward was absolutely necessary in order that improvements could be noted. The ordinary method of judging the product by the "feel" left much to be desired and it was recognized that the personal equation had to be eliminated as much as possible if anything of real value were to result. The most natural idea was to obtain some means of following the action of the lime step by step. This could not be accomplished with the naked eye and hence the assistance of the microscope was necessary. A review of the literature at hand showed that although considerable work with the misroscope had been done the results were not very satisfactory.

Study of Microscopic Changes in Hides During Their Conversion Into Leather.

Some of the earliest work on the cutting of sections of leather was done by Kathreiner in 1879.[4] This work was never published and on inquiring of Prof. Procter it was found that although notes had been preserved, they were in no shape to allow of their being published. Thus we have no authentic record of his work. The next reference found was to some work by Prof. Thomas Palmer.[5] He applied his method to determine the penetration of vegetable tanning agents. The sections were mostly cut by hand. Some sections after dehydration in alcohol and clearing in clove oil were infiltrated with "Strickers" solution (gum arabic and glycerine 3 : 1) and cut with a microtome. In some cases he also dehydrated in alcohol two or three hours, cleared in a mixture of cedar oil and benzol infiltrated in a mixture one part 50° melting point and two parts 40° melting point paraffine until transparent, and then changed to a bath of two

[4] Procter's Leather Industries Laboratory Book, p. 424.

[5] *Collegium*, 1902, p. 325.

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parts 50° melting point and one part 40° melting point paraffine for three or four hours. The mixture of cedar oil and benzol was in the ratio of three to five. He does not tell of any changes noted in the leather except that the distance to which the tanning agent had penetrated could be noted by differential stains, nor does he give the thickness of the sections cut. Procter, in his Leather Industries Laboratory Book, also speaks of cutting sections by hand and of cutting sections by means of a microtome, but gives no directions.

M. Henri Boulanger in an elaborate monograph, "Essais du Cuir dans ses Applications industrielles. Memoires publies par la Societe d'Encouragement pour l'industrie national 1907," part of which is published as "Etude Micrographie du Cuir" in *Bulletin de la Societe d'Encouragement* in 1908, gives some directions for cutting sections. The pieces to be cut are placed 12 hours in a mixture composed of distilled water 5 grams, pharmaceutical glycerine 5 grams, acetone 90 grams. They are then dried and imbedded in hard paraffine and cut. Another method given is to dehydrate in gradually increasing alcohol until absolute is used, to place in xylol, then in melted paraffine 38° to 40°. After several days the tissues are cooled, dried 36 or 48 hours, imbedded in hard paraffine and cut. Although many sections were prepared their thickness is not mentioned. One interesting conclusion of the author is that the elastic fibers are well preserved and that to them the leather owes its strength and pliability, while the connective tissue has been totally changed. This is a remarkable conclusion when one takes into consideration that less than 3 per cent. of the skin is elastic tissue and more than 95 per cent. is connective tissue.[6] Moreover the elastic fibers have little elasticity and are the first to rupture when the skin is stretched. Their chief function appears to be that of support.[7]

Andreis, in an article on "The Process of Liming"[8] speaks of "taking a transverse section of the hide and noting no horizontal layers or channels." He does not give any methods for cutting the sections and presumably means that they are to be cut by hand.

[6] Reimer, *Ding. Poly. Jour.*, No. 205, p. 149 (1872).

[7] Hyde, Diseases of the Skin, p. 22 (1909).

[8] JOURNAL, Am. Leather Chem. Assoc., Vol. VII, p. 609 (1912).

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As none of the references quoted gave definite, concise and adequate directions for preparing sections, experiments were resorted to, in order to find a way to prepare good sections by some simple and quick method. Having no landmarks to guide us, much time was spent in going astray. At this time certain sections of rocks were being made by grinding and this method appeared feasible for leather. The piece of leather to be ground was placed in Canada balsam in a tube in hot water and suction applied. After two to four hours the leather seemed impregnated with balsam and was removed, mounted on a piece of plate glass 1 inch square and ground with a carborundum wheel until a flat surface was obtained. The piece was then turned over and mounted and the grinding continued, until the section was fairly thin. Then a finer wheel was used, until the section became very thin. It was removed, turned over and mounted on a glass slide and the grinding resumed, until the section was as thin as could be obtained. These sections showed some fiber bundles but were unsatisfactory in three ways. The process was too slow, the sections too thick, and a complete section could not be obtained as some parts were always torn away in grinding.

Methods of Imbedding and Cutting Tissues.

Leather is harder and tougher than ordinary tissue. It is dense and requires an unusually long period of infiltration. It is tough and offers great resistance to the knife so that the infiltration must be very thorough before good sections can be obtained.

Methods of cutting sections after imbedding in paraffine and celloidin and after freezing were studied. Various modifications were tried and those giving best results are described in detail, although they are merely modifications of methods used in pathology.

The method of imbedding in paraffine involves the following steps.

1—95 per cent. alcohol 24 hours, change after 12 hours.
2—Absolute alcohol 24 hours, change after 12 hours.
3—Xylol, 1 hour.
4—Xylol, 2 hours.
5—Paraffine 42° melted in an oven from 12 to 24 hours depending on size of piece used.
6—Paraffine 52° from 24 to 48 hours depending on size of the piece.

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The piece is then taken from the molten paraffine and imbedded according to the following procedure. A small dish is greased with tincture of green soap or glycerine and placed in cold water. Clean 52° paraffine is melted with a free flame and the molten paraffine is allowed to drop into the dish until it has attained a depth greater than the thickness of the piece to be imbedded. As soon as a film of hardened paraffine has formed on the bottom the tissue is removed from its previous bath and placed face down in the dish. The surface of the melted paraffine is now cooled by blowing on it, and as soon as a fairly thick film has formed the whole dish is plunged into ice water.

In spite of all precautions taken this method was not satisfactory. If an attempt was made to cut thick sections the tissue tore loose from the imbedding material. If an attempt was made to cut thin sections they either pulled loose or tore. In fact, no complete thin section could be obtained by this method. Other methods based on paraffine infiltration using acetone, clove oil, oil of bergamot and aniline were tried and the results were unsatisfactory. Even infiltration with paraffine in solution, that is, in benzol or xylol, gave poor results. This seems to show that ordinary methods cannot be used and that methods like the one used by Boulanger[9] "infiltrating in melted paraffine 15 minutes and then blocking in hard paraffine" cannot give good results.

The next method tried was the celloidin method. In this the dehydration was carried over a longer period so that the presence of any moisture was precluded. The procedure was as follows:

1—80 per cent. alcohol 12 hours.
2—95 per cent. alcohol 48 hours, changed every 24 hours.
3—Absolute alcohol 48 hours, changed every 24 hours.
4—Absolute alcohol and ether (equal parts) 24 hours.
5—1 per cent. celloidin 96 hours.
6—2 per cent. celloidin 120 hours.
7—5 per cent. celloidin 168 hours.
8—10 per cent. celloidin 6 days to 2 weeks depending on the size of sample used.

In order that a number of pieces might be imbedded simultaneously they were held in clips tied to strings, which led through holes, in the wooden cover of a shallow dish. This dish was filled

[9] Bulletin de la Societe d'encouragement, p. 250 (1907).

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with a 10 per cent. solution of celloidin, the cover put on and the ether and alcohol allowed to evaporate. The tissues were then cut out, trimmed and mounted on wooden blocks. They were cut in a microtome under a constant flow of 80 per cent. alcohol. The sections obtained by this method, after long practice, were as thin as 5 or 7 microns and averaged about 10 to 18 microns. These could be examined even with an oil immersion lens. This method while giving excellent results had as a very serious disadvantage the long time necessary for good results. Many attempts were made to shorten this method but none gave good results. A very long time is absolutely necessary for perfect infiltration.

Believing that the added knowledge gained by experience might after all, enable us to use the paraffine methods, these were again tried. The results while better than those first obtained, still left much to be desired. The leather tore away from the paraffine very easily and it was impossible to cut good sections. The paraffine methods had so many advantages both as to quickness and simplicity, that many modifications of the method previously given, were repeatedly tried. The conclusion finally reached was, that none of the paraffine methods would give good results. Methods using beeswax, gum arabic, etc., were tried and also failed to give good results.

The only short method which appeared promising was the freezing method and this was then tried. This method had the obvious advantage of great saving in the time required to obtain complete sections. The method was was very simple and, although much practice and experience were necessary before good sections were obtained, the results justified the time spent in acquiring the technique. The sample to be sectioned was cut from calfskins, 1 by 2 centimeters and if wet, mounted directly. If dry, they were first soaked in water until thoroughly moistened and then mounted upon the base plate of a Bardeen microtome and covered with a thick solution of gum arabic. The liquid carbon dioxide was then turned on and the pieces were frozen very gradually. When the right degree of hardness has once been obtained the piece should never be allowed to warm up and should never be frozen again. This is of great importance as several

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freezings will cause important changes in the structure.[10] The greatest changes are caused by over freezing and if this is done excessively, the piece used may crumble and become worthless. A slight fixation of the tissue in 10 per cent. formol[11] prevents most of the changes due to freezing. The sections when cut are placed in a dish filled with water. They are then transferred by means of a brush or section lifter to a 10 per cent. dextrin solution which is kept warm, and floated onto a glass plate, dried a few minutes, soaked in absolute alcohol until clear and coated by pouring over them a 1 or 2 per cent. solution of celloidin. The plates are placed in warm water and left until the thin celloidin sheet floats off. They can now be handled easily and quite roughly without any danger of damage. They can be stained with alcoholic or aqueous solutions of various dyes. A water solution of eosin and also a double stain, first in Weigert's haematoxylin and then in Van Giesens[12] mixture were used. The latter gave excellent results and enabled one to distinguish the various kinds of fibers present, with great certainty.

The sections were not so thin as those obtained by the celloidin method, averaging only 35 to 40 microns, but this was thin enough to allow the use of any high power objectives except the oil immersion. The sections were very delicate and required great care in the preliminary handling. The method requires little time. A skilled operator can fix, freeze, stain and mount a complete section in 30 or 40 minutes. In some cases the time required is greater depending on the ease with which the piece in question can be cut. Sections from heavy hides during the liming require much longer, as the tissue is very delicate and flabby and tears very easily. After the hide has been in a tan liquor it can be cut very rapidly. This method has not only the advantage of speed but also is better in that the tissue is practically the same as it was before cutting. The method does not subject the tissue to such severe treatment as for instance the dehydration with absolute alcohol, which is necessary in the case of the celloidin and paraffine methods. It is true that freezing may dehydrate in a certain sense, but the following immersion in water probably

[10] Warthin Practical Pathology, p. 215.
[11] Warthin Practical Pathology, p. 216.
[12] Warthin Practical Pathology, p. 260.

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allows the tissue to resume its previous condition. This seems logical, since the freezing lasts a very short time, from 5 to 10 minutes at the most.

Study of Changes in Structure During Tanning.

Before proceeding to the experimental study of tissues prepared in the laboratory a considerable number of commercial products were examined. Sections were made of various commercial leathers such as dongola, waterproof, wax upper, plow grain, flesh splits, badger sides, oil grain, reliance calf, dull romar sides, kangaroo calf and others. These gave some idea of how a finished leather looked. Through the courtesy of Mr. Carl E. Schmidt of Detroit, pieces were cut daily from a particular calfskin as it went through his tanning process and sent for examination. As soon as these samples were received a section was made by the freezing method and a piece started by the slow celloidin method. This set was kept as a standard of a good product and will be referred to as S-22. This set did not, however, entirely fulfill its purpose, because the necessity of knowing the exact location and orientation of the pieces cut from the hide was not discovered until later. This was shown by an examination of pieces cut in a systematic manner from a finished calfskin (Experiment S-18). Samples were taken from this leather at the butt, right and left flank, and neck and carefully infiltrated with celloidin. Sections were cut both parallel and at right angles to the grain. The sections showed a great difference in structure between pieces cut from the flank and from the butt. These show the flank to have a much smaller amount of connective fibers than the butt and neck. Moreover, the fiber bundles of the flank are further apart and in general form a looser network. The connective tissue is more wrinkled that is, the folds in the individual fiber bundles are more numerous. This apparently accounts at least partially for the looseness of the flank after tanning.

This difference between various portions of the same skin was further studied in series S-26, by tanning two pieces of calfskin cut so that one piece was almost entirely flank while the other was along the backbone. Small pieces were cut daily from adjacent portions of each skin, one from the backbone and the other

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from the edge of the flank, and sections were prepared by the freezing method using the Van Giesen stain. Sections were cut both parallel and at right angles to the backbone in each instance. These showed the same looseness in structure in the fresh flank as was evident in the finished leather.

This subject was pursued still more systematically in Series S-36 where a whole calfskin was trimmed to an approximate rectangle and divided into six pieces. This work is referred to again in the discussion of volume changes where the details are given.

Through the courtesy of V. A. Wallin of Grand Rapids, samples of a certain cow hide were sent throughout the tanning process. The pieces were taken so that the sections made therefrom could be cut parallel and at right angles to the backbone. Samples were received during the following stages of the tanning process. All sections were cut by the freezing method.

No. 1.—Washed hide—originally a green salted one.
No. 2.—After 24 hours in lime.
No. 3.—After 72 hours in lime.
No. 4.—After 96 hours in lime.
No. 5.—Out of hot water.
No. 6.—Into cold water.
No. 7.—Out of cold water.
No. 8.—Out of rockers—in 8 days.
No. 9.—Out of hang yard—in 4 days.
No. 10.—Out of first layer—in 5 days.
No. 11.—Out of second layer—in 9 days.
No. 12.—Out of third layer—in 15 days.
No. 13.—Out of fourth layer—in 22 days.
No. 14.—Out of fifth layer—in 28 days.
No. 15.—Out of wet dip—in 15 days.
No. 16.—Out of tempering vats—in 2 days.
No. 17.—Out of bleach.
No. 18.—Out of oil wheel.
No. 19.—Finished leather.

In these various experiments about 125 different blocks were prepared, from which 600 specimens were cut, stained and mounted. A careful examination of all these sections gave, however, rather meager results. The changes from day to day are so gradual and the differences in structure of different portions of the same hide are so pronounced that it is extremely difficult

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to state the cause for any differences observed. The fiber bundles become partially separated into fibrils in the liming process, but it could not be determined whether these fibrils are hollow or solid. In the bark-tanned process the interstices become filled with solid material so that the leather becomes firm and of more uniform structure. In chrome-tanned leather, the interstitial spaces are even greater than in the soaked hide and the fiber bundles and fibrils are sharply defined. The flank is undoubtedly composed of larger fiber bundles than the butt or shoulder and in the former there are larger spaces between these bundles than in the latter.

The idea first held that the microscopic method could be used in the tannery, as an accurate check on the process, had to be abandoned. The great difficulty was that in a given skin, pieces from different parts showed such differences in structure that even after long experience one could not tell whether the differences shown were inherent in the skin or due to the influence of the treatment.

Changes in Volume of Hides During Liming Process.

Changes in the volume of hides in the limes are so great as to be readily noticed. There have, however, been no quantitative data published on this point. The apparatus used for these measurements is shown in Fig. 1.

It consists of a brass cylinder *A*, 2.5 inches in diameter and 15 inches high. At the bottom a small brass tube *B*, 0.25 inch in diameter leads to an upright 100 cc. glass stoppered burette, *C*. The cover *D* screws on to the cylinder by means of a very fine thread, which insures a water-tight joint. The cover is divided into 30 equal divisions on the edge *K* and a vertical mark is made on the cylinder, permitting the cover to be screwed down to a definite point or reading. In the center of the cover a hole is bored into which a pipe with outside threads *E* is soldered. Another pipe with inside threads *F* fits over *E*. A glass tube *G* with a fine string around it is inserted into *E* through *F* and screws tight by means of *F*. This joint is also water tight, if the thread has been previously greased. The threads of cover *D* are also greased, anhydrous lanoline proving a good material for this purpose. The glass tube *G* has a mark, to which the liquid

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used is allowed to ascend before a reading is taken. This is done by keeping burette *C* filled to a mark, higher than the top of the cylinder. The cylinder is lacquered on the inside and can be used for lime.

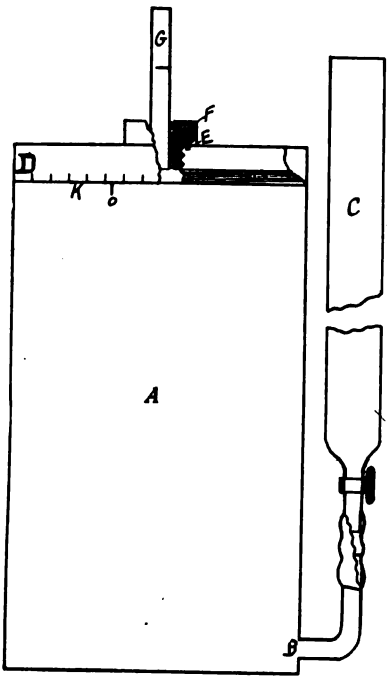

FIG. 1.

To obtain some idea of the accuracy of the measurements made, the following experiments on the volume of a glass stopper are given:

Number of test	I	II	III	IV	V
Zero reading in cc.	25.45	58.9	20.70	59.85	57.65
Taken out in cc.	50.00	0.0	50.0	0.0	0.0
Total cc.	75.45	58.9	70.70	59.85	57.65
Final reading	34.50	17.9	29.95	18.90	16.65
Volume in cc.	40.95	41.00	40.75	40.95	41.00

The average volume was 40.93 cc. and the maximum error was 0.18 cc. in 40.93 cc. equaled 0.44 per cent. This error, however, was relatively small because the stopper could be dried and

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always brought to a certain condition of surface moisture, not a varying one, as was the case with skins. The removal of liquid which was made necessary whenever the volume exceeded about 50 cc. was best accomplished by means of a pipette. The liquid was drawn up into the burette after a measurement had been taken, by means of a rubber tube attached to the burette and to a suction pump. The procedure was as follows: Some of the liquid to be used was put into the cylinder *A* and the burette filled by applying suction. The stop cock was closed, the cylinder filled and the cover screwed down to a certain mark. The stop cock was then opened and the liquid allowed to run into the cylinder until the meniscus in the glass tube *C* was even with the mark. A reading of the burette gave the zero reading. The liquid was sucked back into the burette, the cover taken off, the sample placed in the cylinder and, if the volume was large, some of the liquid was pipetted off. The cylinder was then closed and a reading taken as before. This gave a final reading and from it and the zero reading the volume was easily calculated. The skin to be measured was always dried with a moist cotton cloth which was wrung as dry as possible. The skin was always measured in the same liquid in which it was at that stage of the experiment, that is, when in the limes, in lime water; when in pickle, in pickle solution, etc. Duplicate determinations on pieces of skin whose volume was from 200 to 400 cc. agreed within about 1 cc. When dry skins were to be measured the cylinder was filled with water. The skin naturally absorbed some water, but if the experiment was performed rapidly, the error was not large, as is shown by the following experiment:

Zero reading	56.75	
Final reading	14.25	
Volume	42.50	after 1 minute
	42.65	after 2 minutes
	42.85	after 3 minutes
	42.70	after 4 minutes
	42.95	after 5 minutes
	43.00	after 10 minutes
	43.1	after 15 minutes
	43.3	after 20 minutes

The change in volume due to water absorption is very small.

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To test the absolute accuracy of the method this same piece of skin was dried and its volume remeasured. The agreement was within 0.5 cc. One difficulty to be guarded against in measuring dry skins is the tendency of air bubbles to adhere to the hairs. This can be avoided by shaking the whole apparatus just prior to taking measurements.

EXPERIMENTAL WORK ON VOLUME CHANGES OF CALFSKINS.

Nine sets of tests involving measurements of volume changes on twenty-one different pieces of skin are reported here. Microscopic sections from some of these sets have been referred to previously. The full data are given under the separate headings, but the sets may be outlined as follows:

S-25—A half-calfskin split along the backbone and trimmed, cut into three pieces of about equal size at right angles to the backbone. Carried through the tanning process. Changes in weight of the pieces were also noted and the density at each stage computed.

S-26—A half calfskin as above was carried through the whole process as one unit. Measurements of surface area and weight were included.

S-27—A piece of calfskin carried through the limes only.

S-28—Duplicate of 26.

S-29—A half calfskin was cut parallel to the backbone to make one piece back and the other flank. Carried through the limes.

S-31—Duplicate of 29, but carried only through soaking process.

S-36—A whole calfskin trimmed and cut into six pieces. Protective action of lime soap tested.

S-39—Duplicate of 25.

S-39B—Duplicate of 29.

EXPERIMENT S-25.

A dry salted calfskin was split along the backbone and one half was trimmed and cut into three pieces of about equal size at right angles to the backbone. The piece nearest the head is marked I, the middle piece II, and that nearest the tail III. These pieces were soaked in water three days, the water being changed every 12 hours. They were then placed in limes and made by using 5

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grams of slaked lime to 400 cc. of water, a portion of old lime being added to inoculate the new lot. It was bated in a bran drench and pickled in salt and sulphuric acid solution made by taking 3 grams of concentrated sulphuric acid and 36 grams of salt in 850 cc. of water. The tannage was by Dennis's one-bath chrome method. In the following tables and curves the changes in volume and weight are calculated on the volume and weight of the skin after 72 hours soaking in water instead of on the dry skin. This follows the usual custom of basing all computations on the wet hide and allows comparison to be made with green hides.

EXPERIMENT S-25.—CHANGES IN DENSITY.

Condition of skin.	Number I	Number II	Number III
In water 72 hours.....	1.08	1.10	1.12
In lime 24 hours.....	1.09	1.10	1.13
In lime 48 hours.....	1.08	1.06	1.06
In lime 72 hours.....	1.08	1.09	1.05
In lime 96 hours.....	1.05	1.05	1.03
In lime 120 hours.....	1.06	1.07	1.04
In lime 144 hours.....	1.0	1.0	1.10
In lime 168 hours	1.07	1.08	1.09
In lime 192 hours.....	1.07	1.07	1.08
Unhaired and fleshed ...	1.07	1.05	
Bated	1.04	1.03	
Pickled	1.06	1.06	
Tanned	1.06	1.07	

EXPERIMENT S-26.

A dry salted calfskin was trimmed and split along the backbone. It was intended to carry a half-skin through the experiment as one piece but the apparatus for volume measurements was found to be too small so it was split into two pieces. The figures for the two pieces have been added together so that the result is reported as if it had been kept as one piece. Measurements are reported on volume, weight, area and density throughout the tanning process. These pieces were soaked for 24 hours in water, the latter being changed after 12 hours. The lime used was made by dissolving 5 grams of dry hydrated lime in 400 cc. of water. The pieces were placed in this solution for ten days. The lime was changed every 48 hours and a new lime of the same concentration was prepared. After liming until the hair slipped easily, the skins were placed in warm water for a few minutes, unhaired and fleshed.

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EXPERIMENT S-25.—CHANGES IN WEIGHT.

Condition of the skin	Number I			Number II			Number III		
	Weight in grams	Increase in grams	Per cent. increase	Weight in grams	Increase in grams	Per cent. increase	Weight in grams	Increase in grams	Per cent. increase
In water 72 hours.....	90.0	0.0	0.0	85	0.0	0.0	86.7	0.0	0.0
In lime 24 hours.....	120.0	30.0	33.3	99	14.0	16.5	110.0	23.3	26.7
In lime 48 hours.....	124.0	34.0	37.8	103	18.0	21.2	116.0	29.3	33.8
In lime 72 hours.....	129.0	39.0	43.3	110	25.0	29.4	123.0	36.3	41.9
In lime 96 hours.....	132.0	42.0	46.7	114	29.0	34.1	129.0	42.3	48.8
In lime 120 hours.....	130.0	40.0	44.5	112	27.0	31.7	125.0	38.3	44.2
In lime 144 hours.....	136.0	46.0	51.1	111	26.0	30.6	134.0	47.3	54.6
In lime 168 hours.....	138.0	48.0	53.3	111	26.0	30.6	138.0	51.3	60.6
In lime 192 hours.....	138.5	48.5	53.9	112	27.0	31.8	134.0	47.3	54.6
Unhaired and fleshed..	105.0	15.0	16.7	92	7.0	8.2	—	—	—
Bated.....	135.0	45.0	50.0	102	17.0	20.0	—	—	—
Pickled.....	123.0	33.0	36.7	102	17.0	20.0	—	—	—
Chrome tanned	124.0	34.0	37.8	104	19.0	22.4	—	—	—

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EXPERIMENT S-25.—CHANGES IN VOLUME.

Condition of the skin	Number I			Number II			Number III		
	Volume in cc.	Increase in cc.	Per cent. increase	Volume in cc.	Increase in cc.	Per cent. increase	Volume in cc.	Increase in cc.	Per cent. increase
Dry salted	32.2	—51.0	—61.3	27.7	—50.0	—64.4	26.4	—50.7	—65.8
In water 18 hours	66.7	—16.5	—19.8	56.7	—21.0	—27.0	—	—	—
In water 72 hours	83.2	0.0	0.0	77.7	0.0	0.0	77.1	0.0	0.0
In lime 24 hours	110.6	27.4	32.7	90.0	12.3	15.8	97.4	20.3	26.3
In lime 48 hours	114.4	31.2	37.5	97.4	19.7	25.4	109.9	32.8	42.5
In lime 72 hours	119.8	36.6	40.0	101.0	23.3	30.0	116.9	39.8	51.6
In lime 96 hours	125.9	42.7	51.3	108.3	30.6	39.4	125.0	47.9	62.1
In lime 120 hours	122.7	39.5	47.5	105.2	27.5	35.4	120.7	43.6	56.6
In lime 144 hours	127.2	44.0	52.9	102.4	24.7	31.8	121.9	44.8	58.1
In lime 168 hours	129.0	45.8	55.0	102.3	24.6	31.7	126.8	48.7	63.2
In lime 192 hours	129.2	46.0	55.3	104.3	26.6	32.2	124.7	47.6	61.7
Unhaired and fleshed	98.2	15.0	18.0	87.5	9.8	12.6	—	—	—
Bated	130.4	47.2	56.7	98.8	21.1	27.2	—	—	—
Pickled	116.2	33.0	41.0	96.2	18.5	23.8	—	—	—
Chrome tanned	117.5	34.3	41.2	97.5	19.8	25.5	—	—	—

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EXPERIMENT S-26.—CHANGES IN VOLUME, WEIGHT, AREA AND DENSITY.

Condition of the skin	Volume in cc.	Increase in cc.	Per cent. increase	Weight in grams	Increase in grams	Per cent. increase	Density	Area in sq. in.
Dry salted	148.7	—219.6	—56.9	170	—235	—58.0	1.14	198
In water 24 hours	368.3	0.0	0.0	405	0.0	0.0	1.10	252
In lime 24 hours	500.6	123.3	34.3	543	138	34.1	1.09	254
In lime 48 hours	535.4	167.1	43.3	572	167	41.3	1.07	254
In lime 72 hours	566.8	198.5	51.4	600	195	48.2	1.06	256
In lime 96 hours	570.2	201.9	52.3	605	200	49.4	1.06	249
In lime 120 hours	581.3	213.0	55.2	613	208	51.4	1.05	249
In lime 144 hours	582.0	213.7	55.3	626	221	54.6	1.08	250
In lime 168 hours	610.2	241.9	62.6	643	238	58.8	1.05	250
In lime 192 hours	606.3	238.0	61.6	650	245	60.5	1.07	248
In lime 216 hours	614.7	246.4	63.8	657	252	62.3	1.07	246
In lime 240 hours	605.5	237.2	61.4	650	245	60.5	1.07	245
Unhaired and fleshed	407.9	39.6	10.3	436	31.0	7.7	1.07	242
Bated	384.6	16.3	4.2	404	—1.0	—0.5	1.06	247
Pickled	335.2	—33.1	—8.6	374	—31	—7.7	1.12	249
Chrome tanned	347.3	—21.0	—5.4	382	—23	—5.8	1.10	209*

* This figure for area is of the dry leather.

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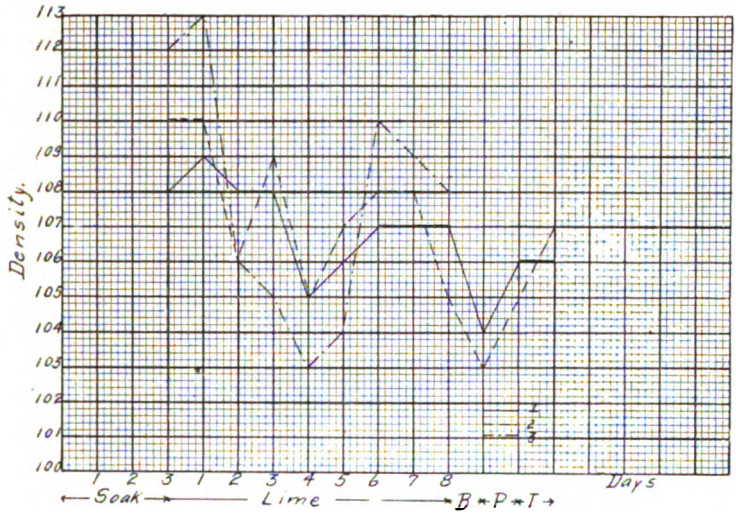
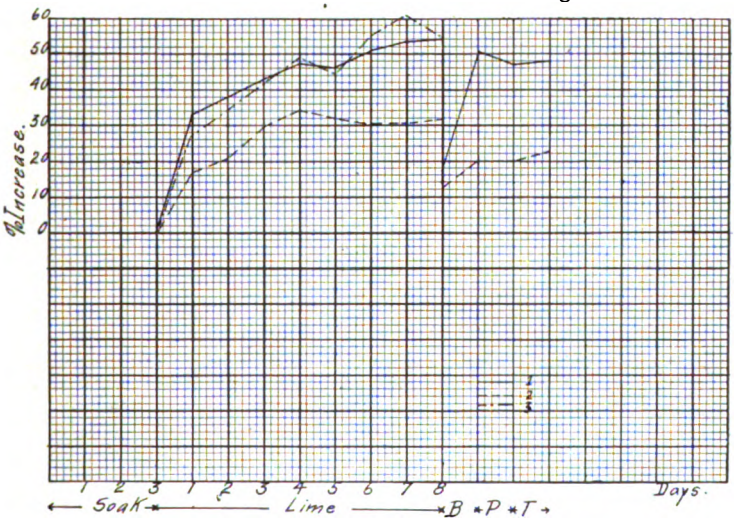
EXPERIMENT 25.—DENSITY.



EXPERIMENT 25.—WEIGHT.

Per cent. increase on third soaked weight.



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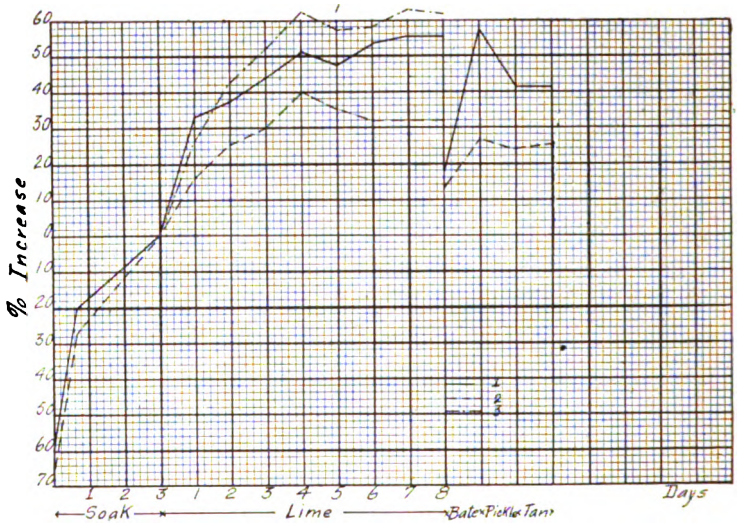
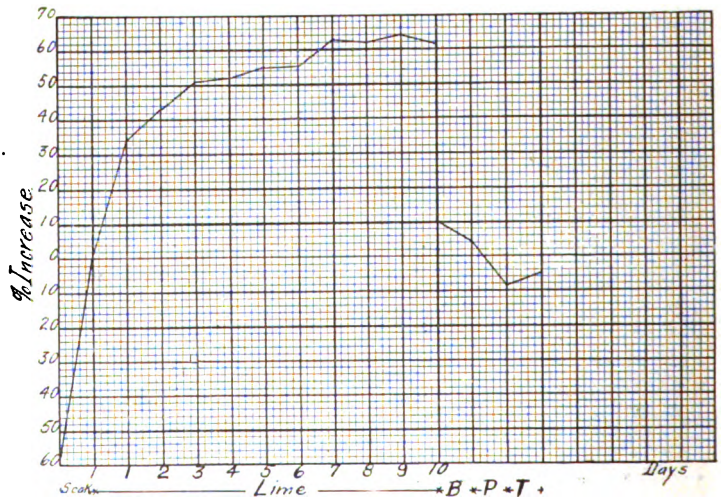
EXPERIMENT 25.—VOLUME.
Per cent. increase on third soaked volume.



EXPERIMENT 26.—VOLUME.
Per cent. increase on 24-hour soaked volume.



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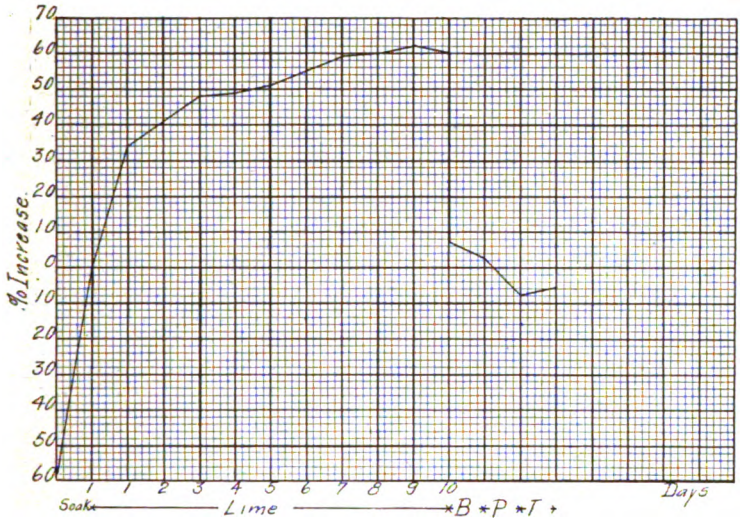
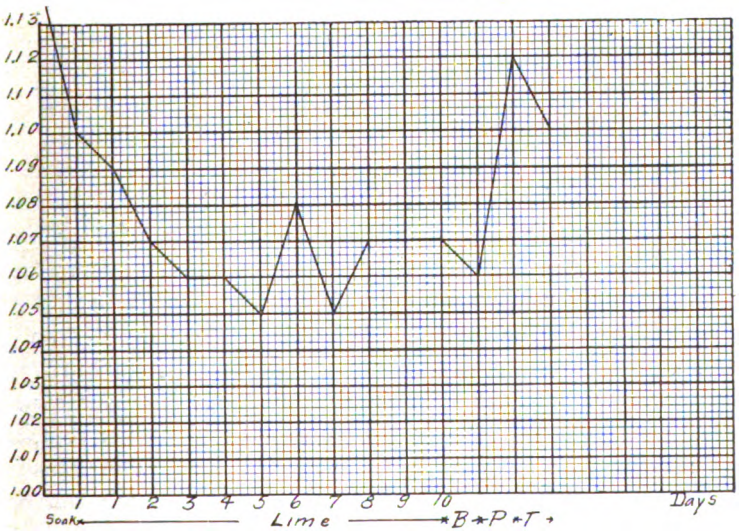
EXPERIMENT 26.—WEIGHT.
Per cent. increase on 24-hour soaked weight.



EXPERIMENT 26.—DENSITY.



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The samples were bated three hours in a solution of tenth normal lactic acid, in a drum. They were pickled about five hours in an N/50 solution of salt and sulphuric acid. They were then placed in a drum with a normal salt solution for one hour and chrome-tanned by the one-bath process. Sections were also cut daily during this series, as has been mentioned in the discussion of the microscopic study. The results are given in the accompanying table and curves.

Experiment S-27.

In this test a piece of dry salted calfskin was used. It was soaked in water 24 hours. The water was changed after 12 hours. A lime solution containing 5 grams of slaked lime in 400 cc. of water was used to unhair the skin. The hide was in the limes seven days. Sections and volume measurements were made daily and the results tabulated.

EXPERIMENT S-27 CHANGES IN VOLUME, WEIGHT AND DENSITY.

Condition of the skin	Volume in cc.	Increase in cc.	Per cent. increase	Weight in g.	Increase in g.	Per cent. increase	Density
Dry salted.....	83.3	—154.6	—65.0	92	—169	—64.7	1.10
In water 24 hours.	237.9	0.0	0.0	261	0.0	0.0	1.10
In lime 24 hours..	335.6	97.7	41.1	380	119	45.6	1.12
In lime 48 hours..	356.2	118.2	49.8	374	113	43.3	1.05
In lime 72 hours..	354.1	116.2	48.9	365	104	39.9	1.03
In lime 144 hours.	342.4	104.5	44.0	360	99	37.9	1.05
In lime 168 hours.	343.6	105.7	44.5	357	96	36.8	1.04

Experiment S-28.

In this experiment a piece of dry salted calfskin was used. The piece of skin was soaked in water 24 hours, the latter having been changed after 12 hours. The limes used were of the same concentration as in Experiment 26. The pieces of hide were limed 6 days. Volume, weight and area measurements were made daily. The skins were limed, unhaired and fleshed, bated in an N/10 solution of lactic acid and followed by a bran infusion. They were pickled in an N/50 solution of sulphuric acid and salt and tanned by the method given in the previous experiment. The product was fair. Analysis showed 5.6 per cent. ash while a standard sample had 5.0 per cent. ash. The measurements taken are in the following table. The increase and percentage increase in weight and volume are all computed on the volume and weight after 24 hours soaking in water.

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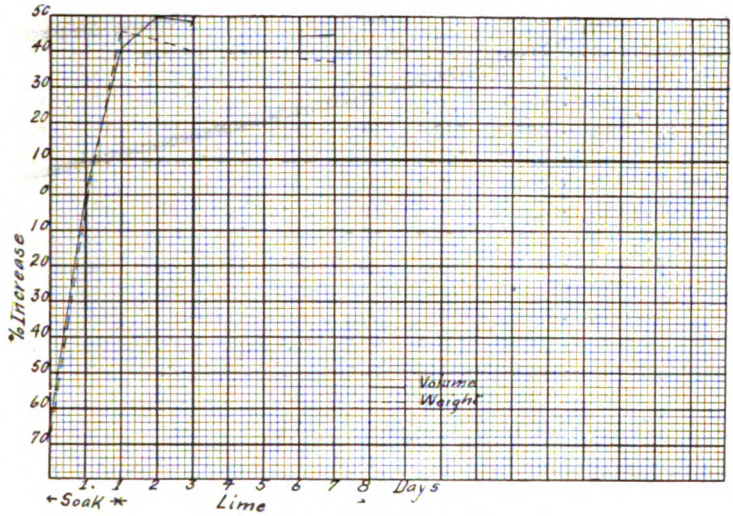
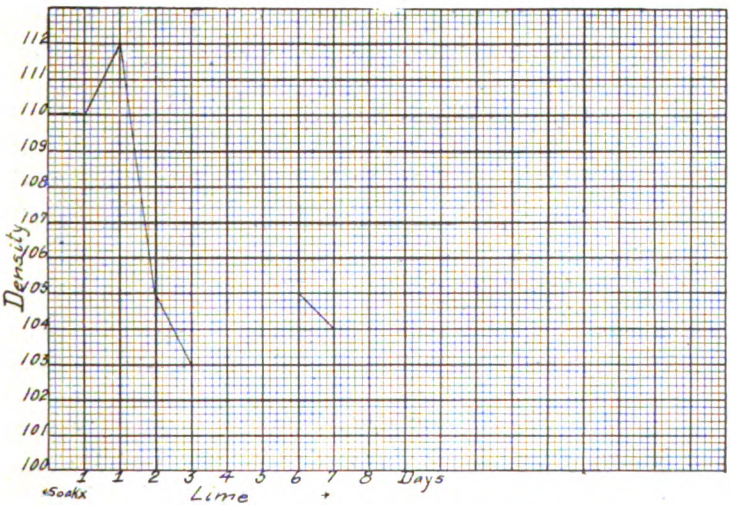
EXPERIMENT 27.

Per cent. increase on 24-hour soaked volume and weight.



EXPERIMENT 27.—DENSITY.



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EXPERIMENT S.28 CHANGES IN VOLUME, WEIGHT, AREA AND DENSITY.

Condition of the skin	Volume in cc.	Increase in cc.	Per cent. increase	Weight in g.	Increase in g.	Per cent. increase	Area in sq. in.	Density
Dry salted	122.6	—181.7	—59.7	135	—191	—58.6	135	1.10
In water 24 hours .	304.3	0.0	0.0	326	0.0	0.0	161	1.07
In lime 24 hours ..	427.2	122.9	40.3	474	148	45.4	161	1.11
In lime 48 hours ..	453.2	148.9	48.8	482	156	47.9	165	1.06
In lime 72 hours ..	454.2	149.9	49.3	483	157	48.1	163	1.06
In lime 96 hours ..	455.1	150.8	49.5	484	158	48.5	164	1.06
In lime 120 hours .	476.0	171.7	56.5	501	175	53.7	164	1.05
In lime 144 hours .	463.0	158.7	52.1	497	171	52.5	160	1.07
Unhaired and fleshed	220.2	— 84.1	—27.6	231	— 95	—29.1	178	1.05
Bated	184.5	—119.8	—39.3	192	—134	—41.1	—	1.04
Pickled	129.3	—175.0	—57.5	145	—181	—55.5	166	1.12
Chrome tanned....	142.5	—161.8	—53.1	158	—168	—51.5	151	1.11

EXPERIMENT S-29.

In order to show whether the flank absorbs more water than the butt, a piece of each kind was used in this experiment. Number one was a piece of calfskin butt and number two, a piece of flank from the same skin. These pieces were always treated in the same manner, in the same solutions. The hides were soaked 48 hours in water, this being renewed every 12 hours. The limes contained 5 grams slaked lime per 400 cc. of water. The liming continued for 4 days and during this time volume measurements were made daily. The results follow:

EXPERIMENT S-29.—CHANGES IN VOLUME OF BUTT AND FLANK.

	Number I, butt		Number II, flank	
Condition of the skin	Volume in cc.	Per cent. increase	Volume in cc.	Per cent. increase
In water 48 hours	87.1	—	134.8	—
In lime 24 hours	126.2	44.8	208.4	54.7
In lime 72 hours	138.2	58.8	244.8	82.2
In lime 96 hours	141.7	62.7	258.4	92.0

EXPERIMENT S-33.

The following experiment was made with pieces of dry salted calfskin. Two pieces were taken; number one being from the flank and number two from the butt. The hides were soaked 24 hours in water, this being changed after 12 hours. The volume was measured before and after soaking.

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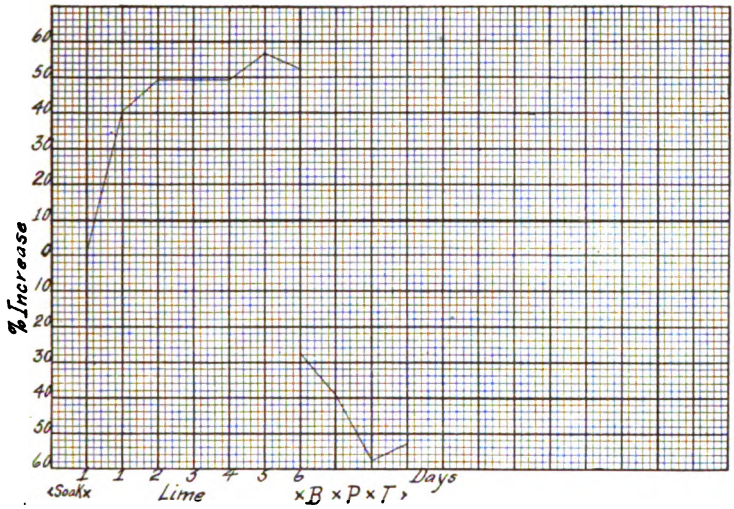
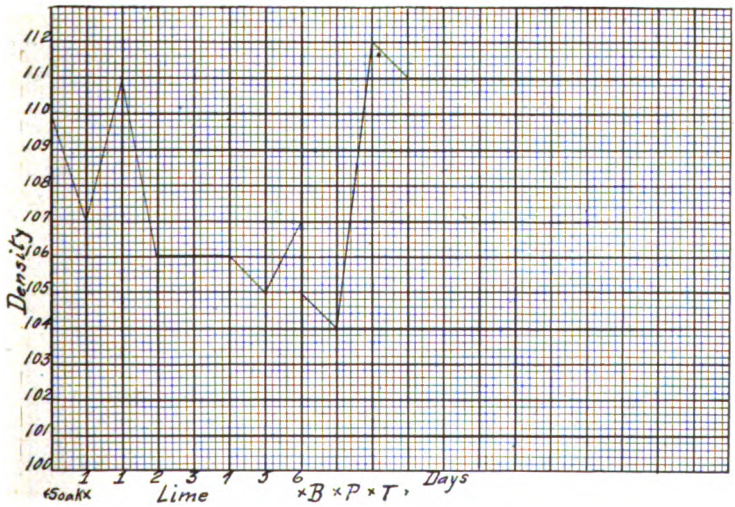
EXPERIMENT 28.—VOLUME.

Per cent. increase on 24-hour soaked volume.



EXPERIMENT 28.—DENSITY.



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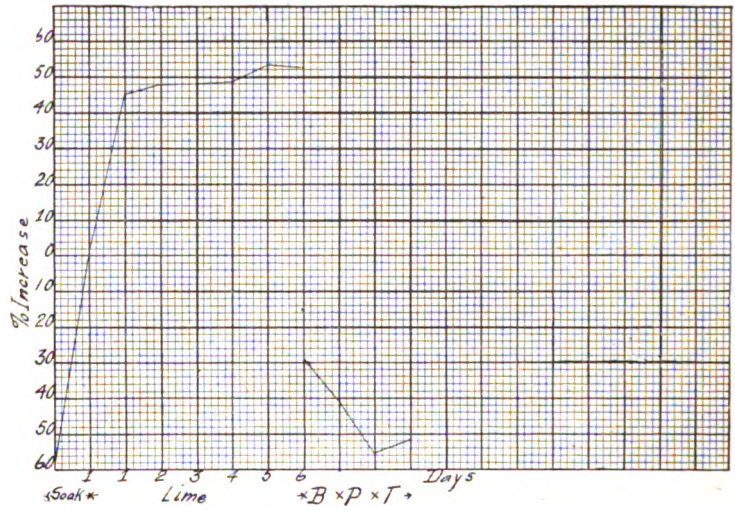
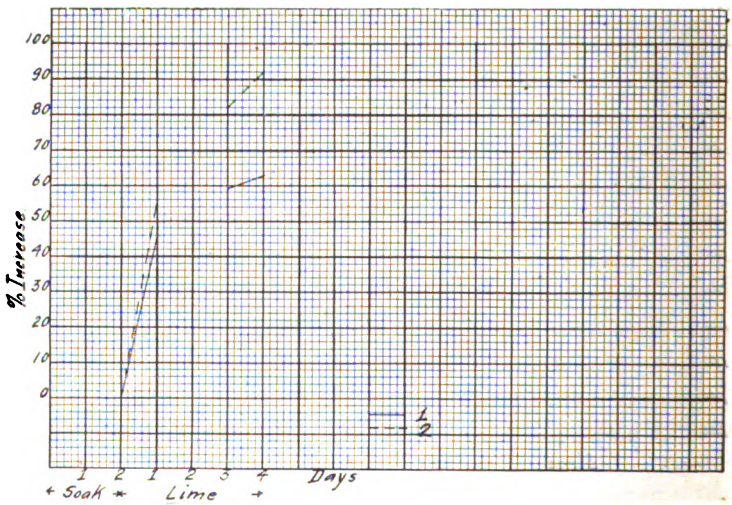
EXPERIMENT 28.—WEIGHT.

Per cent. increase on 24-hour soaked weight.



EXPERIMENT 29.—VOLUME.

Per cent. increase on 48-hour soaked volume.



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EXPERIMENT S-33.—CHANGES IN VOLUME OF FLANK AND BUTT DURING SOAKING.

Number I, butt			Number II, flank		
Condition of the skin	Volume in cc.	Per cent. increase	Condition of the skin	Volume in cc.	Per cent. increase
Dry salted	60.4	—	Dry salted	56.2	—
After 24 hours in water	75.4	25	After 24 hours in water	81.2	45

EXPERIMENT S-39B.

This experiment was made to confirm the results of Experiment S-29. Two pieces of dry salted calfskin were soaked for 48 hours in water, which was changed every 12 hours. The pieces were limed in a solution of 5 grams of lime in 400 cc. of water, for 5 days. They were unhaired and fleshed, bated with lactic acid, pickled with sulphuric and salt, and chrome tanned in the same manner as stated in Experiment S-28. One piece was from the butt, No. 1, the other, No. 2, was from the flank. Volume measurements were taken daily and the results tabulated.

EXPERIMENT S-39B CHANGES OF VOLUME OF BUTT AND FLANK.

	Number I, butt			Number II, flank		
Condition of the skin	Volume in cc.	Increase in cc.	Per cent. increase	Volume in cc.	Increase in cc.	Per cent. increase
Dry salted	45.3	—31.1	—40.7	45.3	—42.5	—48.5
In water 24 hours	72.8	— 3.6	— 4.1	84.4	— 3.4	— 3.9
In water 48 hours	76.4	0.0	0.0	87.8	0.0	0.0
In lime 24 hours	103.8	27.4	35.8	117.5	29.7	33.8
In lime 48 hours	110.2	33.8	44.2	125.9	38.1	43.4
In lime 96 hours	119.1	42.7	55.9	143.2	55.4	63.1
In lime 120 hours	122.5	46.1	60.3	150.2	62.4	71.1
Unhaired and fleshed	61.3	—15.1	—19.8	81.3	— 6.5	— 7.4
Bated	51.8	—24.6	—32.2	68.8	—19.0	—21.6
Pickled	42.0	—34.4	—45.0	52.5	—35.3	—40.2
Chrome tanned	51.5	—24.9	—32.6	62.7	—25.1	—28.6

EXPERIMENT S-39.

This is in general a duplicate of Experiment S-25. Three pieces of dry salted calfskin were limed in a solution of 5 grams of slaked lime in 400 cc. as in previous experiments, and volume and weight measurements made daily. The results follow in table, Experiment S-39. The increase and percentage increase in weight and volume are computed on the weight and volume of the skin after 48 hours soaking in water, respectively.

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EXPERIMENT S-39.—CHANGES IN VOLUME, WEIGHT AND DENSITY OF SHOULDER.

Number I.

Condition of the skin	Volume in cc.	Increase in cc.	Per cent. increase	Weight in g.	Increase in g.	Per cent. increase	Density
Dry salted.....	150.6	—107.7	—41.7	—	—	—	
In water 24 hours.	253.0	—5.3	—2.1	—	—	—	
In water 48 hours.	258.3	0.0	0.0	287	0.0	0.0	1.11
In lime 24 hours..	346.0	87.7	34.0	384	97.0	33.8	1.11
In lime 48 hours..	380.5	122.2	47.3	418	131	45.6	1.10
In lime 72 hours..	422.0	163.7	63.1	455	168	58.5	1.08
In lime 96 hours..	440.0	181.7	70.4	475	188	65.5	1.08
In lime 120 hours.	416.5	158.2	61.3	449	162	56.5	1.08
In lime 144 hours.	429.0	170.7	66.1	472	185	64.5	1.10
In lime 168 hours.	421.0	162.7	63.0	444	157	54.7	1.08
Unhaired and fleshed.....	236.8	—21.5	—8.3	256	—31	—10.8	—1.08

CHANGES IN VOLUME, WEIGHT AND DENSITY OF FLANK.

Number II.

Condition of the skin	Volume in cc.	Increase in cc.	Per cent. increase	Weight in g.	Increase in g.	Per cent. increase	Density
Dry salted.....	105.9	—122.2	—53.5	—	—	—	—
In water 24 hours.	221.1	— 7.0	— 3.1	—	—	—	—
In water 48 hours.	228.1	0.0	0.0	252	0.0	0.0	1.11
In lime 24 hours..	324.0	95.9	42.0	357	105	41.7	1.10
In lime 48 hours..	359.5	131.4	57.4	395	143	56.7	1.10
In lime 72 hours..	375.0	146.9	64.4	412	160	63.5	1.10
In lime 96 hours..	410.0	181.9	79.7	430	178	70.6	1.05
In lime 120 hours.	432.0	203.9	89.4	469	217	86.1	1.09
In lime 144 hours.	395.0	166.9	73.1	435	183	72.6	1.10
In lime 168 hours.	369.5	141.4	62.0	403	151	59.9	1.09
Unhaired and fleshed.....	226.5	— 1.6	— 0.7	245	—7.0	—2.8	1.08

CHANGES IN VOLUME, WEIGHT AND DENSITY OF BUTT.

Number III.

Condition of the skin	Volume in cc.	Increase in cc.	Per cent. increase	Weight in g.	Increase in g.	Per cent. increase	Density
Dry salted.....	86.0	—111.7	—56.5	—	—	—	—
In water 24 hours.	183.8	— 13.9	— 7.0	—	—	—	—
In water 48 hours.	197.7	0.0	0.0	219	0.0	0.0	1.11
In lime 24 hours..	255.0	57.3	29.0	284	65	29.7	1.11
In lime 48 hours..	292.0	94.3	47.6	322	103	47.0	1.10
In lime 72 hours..	300.0	102.3	51.8	334	115	52.5	1.11
In lime 96 hours..	318.0	120.3	60.9	349	130	59.3	1.10
In lime 120 hours.	325.0	127.3	64.4	357	138	63.0	1.10
In lime 144 hours.	327.5	129.8	65.7	362	143	65.5	1.11
In lime 168 hours.	296.0	98.3	49.7	325	106	48.4	1.10
Unhaired and fleshed.....	216.0	18.3	9.3	235	16	7.3	1.09

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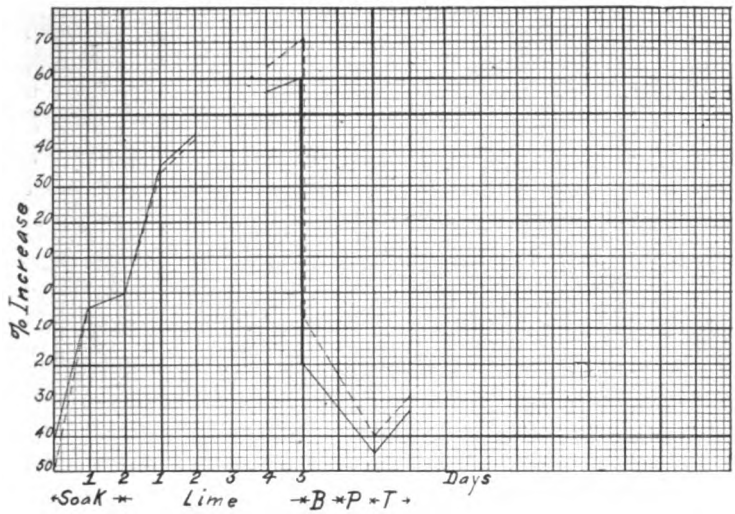
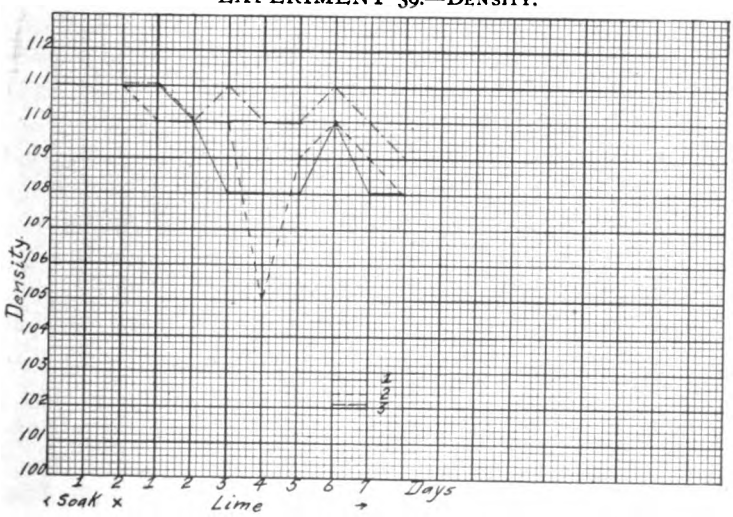
EXPERIMENT 39-B.—VOLUME.

Per cent. increase on 48-hour soaked volume.



EXPERIMENT 39.—DENSITY.



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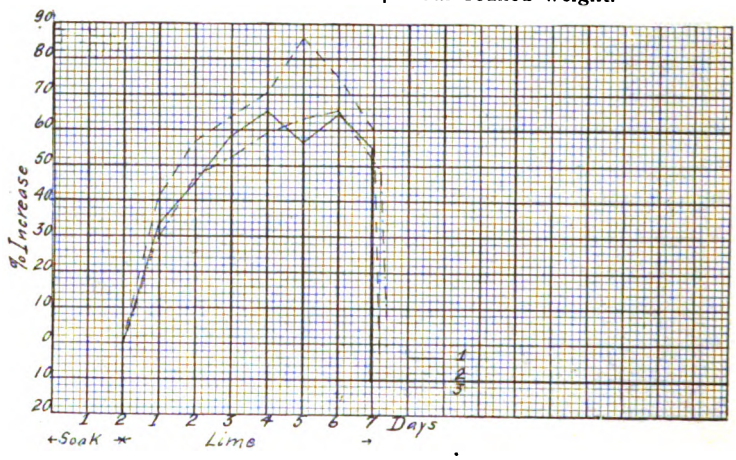
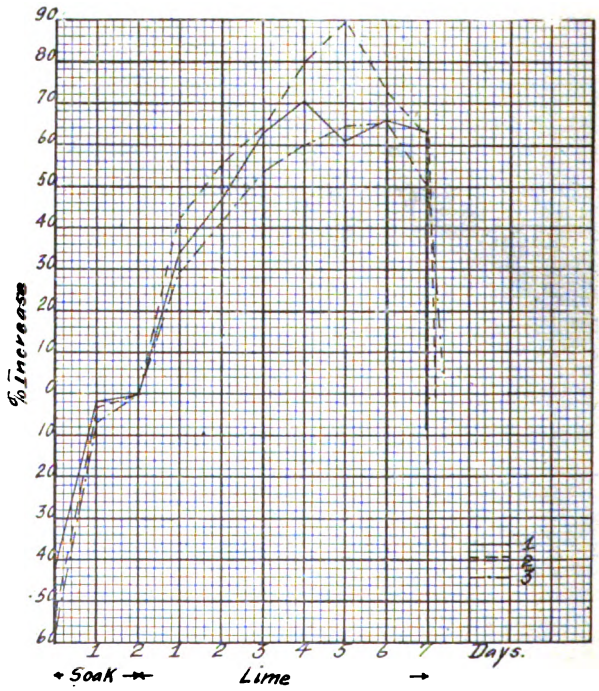
EXPERIMENT 39.—WEIGHT.
Per cent. increase on 48-hour soaked weight.



EXPERIMENT 39.—VOLUME.
Per cent. increase on 48-hour soaked volume.



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Attempts to Prevent Thinness of Flank.

In looking for some remedy for the excessive swelling and subsequent looseness of the flank, the following experiments were made. The reasoning was that the flank was thinner than the rest of the skin and hence had lost more inter-fibrillar substance by solution. If the flank could be protected in some manner this would be partially prevented and the resulting leather should not have so thin and flabby a flank. Some substance had to be used which was easily applied and relatively pliable. The use of aluminum soap was suggested and it was tried. The hides were painted with a hot 10 per cent. solution of aluminum sulphate and left a few minutes. Then the hides were painted with a hot 10 per cent. solution of ivory soap. The pieces were then limed in the usual manner. The results of various experiments follow.

Experiment S-31.—Two pieces of calfskin which had been soaked 24 hours in water were painted thickly with a hot 10 per cent. solution of aluminum sulphate. One of these pieces was immediately placed in milk of lime, the other, after standing 10 minutes, was painted thickly with a hot 10 per cent. solution of ivory soap. A third piece was limed 24 hours, washed thoroughly in water, painted with a hot 10 per cent. soap solution and finally returned to the limes. All three pieces gave the same result so far as could be detected by the ordinary methods of testing the quality of leather. The hair slipped just as easily as in the ordinary cases and the flank was neither fuller nor firmer. The results were negative.

Experiment S-34.—Two pieces of calfskin were taken after 24 hours soaking in water. One was soaped completely three times and then painted three times with an aluminum sulphate solution. The other was soaped and painted once on the flank only. These pieces were limed as usual and sent to the tannery to be chrome tanned and finished. All three pieces apparently gave the same result. No appreciable differences were noticed. The hair slipped just as readily as though the pieces had been limed in the ordinary manner. The leather appeared to have a better grain, but subsequent tests failed to confirm this conclusion.

Experiment S-35.—Eight pieces, which had been soaked 24 hours in water, were painted and soaped, four completely and

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four only on the flank. They were then limed and tanned. After tanning the tests showed negative results. It was impossible to tell by inspection the soaped from the unsoaped area nor did any of the pieces differ apparently from normally limed and tanned skins.

The above experiments were all repeated using a 10 per cent. soap solution only. The moment the hides entered the limes a lime soap was formed. The results of these experiments were almost identical with the previous ones.

The process was studied more quantitatively in Experiment S-36, where in order to study the protective action of soap on various parts of the hide a dry salted calfskin was split down the backbone into two pieces, each of which was again cut at right angles to the backbone into three portions. The pieces on the left side were number 1, 2 and 3 starting at the shoulder and those of the right side, 4, 5 and 6 respectively. The object was to note the various increases in volume and changes in structure occurring in the process. Sections were cut parallel to and at right angles to the backbone, after 48 hours soak, after 96 hours liming and just after removing from the limes. The pieces were cut in each case from a piece of skin taken from the backbone edge and the flank edge of the sample. The samples were subjected to various treatments as follows:

No. 1.—Limed 168 hours in the regular manner.
No. 2.—Limed 144 hours, until flank unhaired easily, but butt not so readily.
No. 3.—Limed 196 hours, 2 days over-limed.
No. 4.—Soaped (10 per cent. solution) all over and limed normally 168 hours.
No. 5.—Soaped flank only and limed normally 168 hours.
No. 6.—Soaped all over and over-limed 2 days, 196 hours in all.

(To be continued.)

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SULPHONATED OILS.

By Dr. Gebhardt Bumcke.

When I saw in the 1914 April number of this JOURNAL that the Provisional Method on Sulphonated Oils was accepted as printed in the December issue 1913, it seemed that many of the methods as given by Benedict, Ulzer, Herbig, Lewkowitsch and others some 10 to 20 years ago were not sufficiently known. Unfortunately the work of the Committee of 1914-1915 through lack of time of its members did not create much improvement of the situation. I do not pretend to bring much new material in the following but mainly a compilation of methods as they were practiced for years in the German government laboratories with such slight changes as have been found to be of some advantage during my 10 years experience.

The Provisional Method for Sulphonated Oils of the A. L. C. A. assumes as total fatty matter the difference between 100 per cent. and the sum of moisture, ash and non-saponifiable. This will lead to errors for the following reasons. The ash will contain only the salts of fixed alkalies while the ammonia and its salts are entirely lost, so is glycerine which is usually present to the amount of ½ to 1 per cent. Sulphates of heavy metals are more or less reduced to oxides in the ash and the loss of SO_3 though small, will also be calculated as total fatty oil. Any loss of unsaponifiable which easily occurs when very light mineral oils are present would also be calculated to the good of the amount of fatty oil. For correct results the direct determination of the total fatty oil is unavoidable. For the estimation or valuation of sulphonated oils the following tests should be made for which I recommend the following methods:

Water Test.—The test is recommended as described in the Provisional Method except that the use of 100 cc. xylol and a flask or Erlenmeyer of 500 cc. is preferable as some oils foam considerably and in order to avoid bumping the glass beads or pumice stone should not be forgotten. By standing over night the xylol gets perfectly clear and any drops of water adhering to the glass can be pushed down by using a feather attached to a wire. The readings should be made at about 70° F.

As the clear xylol when separated from the water in a sep-

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arator is usually used for the next test it is not necessary to further saturate this with water.

Total Fatty Matter.—The amount of total fatty matter is found by dissolving about 4 grams oil (weighed to the second decimal) in 20 cc. water (in a 500 cc. Erlenmeyer) adding a little ammonia to make the solution clear if possible, and 30 cc. diluted hydrochloric acid (1 : 5). After adding some glass beads or pumice stone, boil on reflux condenser until oil and water become clear; this will take about 15 minutes. Cool and transfer to a separator by rinsing with water and sulphuric ether, shake and let settle, draw off the water through a filter, wash the ether layer with water until free from mineral acid and keep the acid and filtered wash waters for determination of SO_3.

Using the above filter after it is air dried the ether is run through it into a flask to let any particles of water settle, funnel and filter are washed with ether and the ether solution transferred into a tared flask, the ether distilled off and the flask dried in the oven, cooled and weighed.

If petrolic ether is used instead of sulphuric ether the unoxidized fatty acids are separated from the oxidized which are not soluble in petrolic ether. Enough petrolic ether (about 150 to 200 cc.) should be used as, if too concentrated the petrolic ether solution of the unoxidized fatty acids is a solvent for the oxidized fatty acids. After the petrolic ether is run off through the filter the same way as above, two more washings of the oxidized fatty acids with petrolic ether follow. These in turn are run through the filter and the filter washed with petrolic ether. The oxidized fatty acids which adhere to Erlenmeyer, separator and filter, are then dissolved in hot alcohol and run through the same filter into a tared flask, the filter and funnel washed with alcohol, the alcohol distilled off and the flask with contents dried, cooled and weighed.

The petrolic ether extract when clear is transferred into a tared flask, distilled, flask and contents dried, cooled and weighed.

Sometimes from a cloudy petrolic ether extract after standing an hour or more, a brown precipitate will settle which represents oxidized fatty acids which have dissolved in the first extraction

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when not enough petrolic ether was used. After rinsing the flask with petrolic ether the brown precipitate is dissolved in alcohol and added to the oxidized fatty acids.

Total SO_3.—The combined acid water and wash water of the preceding test which must be clear, is heated, the SO_3 precipitated with $BaCl_2$ and determined as $BaSO_4$.

SO_3 *in salts,* or combined with ammonia, alkali or heavy metals, is found by weighing 10 grams of sulphonated oil into a separator filled with 20 cc. concentrated NaCl solution adding at least 100 cc. sulphuric ether. Shake well and let settle. If salt water is clear, draw off and repeat three times with 10 cc concentrated NaCl solution. The combined salt water is diluted, a little hydrochloric acid added, heated and the SO_3 precipitated with $BaCl_2$ and determined as $BaSO_4$.

If any oil should show in appreciable quantity after adding HCl and heating, this will remain on the filter or in the beaker, and when filter and beaker are air-dry may be washed out with alcohol (being all fatty acids from sulpho-fatty acids that have dissolved in the brine and were decomposed by heating with the acid).

The alcohol solution is transferred into a tared flask, alcohol distilled off, the flask with contents dried in the oven, cooled and weighed. For each 300 parts of fatty acids 233 parts of $BaSO_4$ are deducted from the amount of $BaSO_4$ found. For Turkey red oils 298 parts of fatty acids correspond to 233 parts of $BaSO_4$.

SO_3 *in sulpho-fatty acids* is found by deducting the SO_3 in salts from the total SO_3. The amount of

Sulpho-fatty acids is found by multiplying the product so obtained by 4.725 for Turkey red oil (sulphonated castor oil) or by 4.75 for other sulphonated oils (80 parts SO_3 correspond to 378 parts ricinol-sulphuric acid, $C_{13}H_{33}O_2.O.SO_3H$, or 380 parts oxy-stearic-sulphuric acid, $C_{18}H_{35}O_2.O.SO_3H$).

The factor 4.75 is sufficiently correct for all oils where the main part of their liquid fatty acids is oleic acid, like olive oil, neatsfoot oil and others. But it is not so reliable for the fish oils which outside of oleic acid contain considerable quantities of other liquid fatty acids like physet-oleic, ($C_{16}H_{30}O_2$); jecoleinic,

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($C_{19}H_{36}O_2$); jecorinic, ($C_{18}H_{30}O_2$); therapinic, ($C_{17}H_{26}O_2$); clupanodonic, ($C_{18}H_{28}O_2$) acid and others.

As these mixtures for the different fish oils are not sufficiently investigated and as it is, without resorting to very complicated methods, impossible to find the molecular formula for the fatty acids of a sulphonated fish oil as they change under treatment, into anhydrides, lactides and esters, it seems for the present time at least the most convenient to accept the factor 4.75 for the fish oils too.

Unsaponifiable.—The unsaponifiable is best obtained either by extracting the saponified neutral oil or the saponified total fatty matter according to Spitz and Hoenig. Ten grams of the sulphonated oil may also be saponified in a 500 cc. Erlenmeyer on reflux condenser with 3-4 grams KOH and 50 cc. alcohol (pumice stone or glass beads not to be forgotten). After 1 hour boiling add 50 cc. water, transfer into a separator, rinse the Erlenmeyer with petrolic ether (boiling point 40-60° C.) use 100 cc. the first and 50 cc. for the following extractions. Extract three times or until no oil spot or ring can be noticed after dropping a few drops of the petrolic ether on paper. Wash the combined petrolic ether extractions with 10 cc. of 50 per cent. alcohol (containing a little phenolphthalein) two or three times or until it shows no more pink color. Transfer into a flask, let it stand until clear, rinse into a tared flask, distil off the petrolic ether, dry, cool and weigh.

As the sulphonated oils during saponification do not always boil smoothly and when extracting with petrolic ether some soaps show that are not soluble in the diluted alcohol but float as white flocks in the petrolic ether, the neutral oil or the total fatty matter is recommended for this test as they both contain all of the unsaponifiable and do not show the difficulties which sometimes occur by using the sulphonated oil itself for this test.

Only if very light mineral oils are present the direct saponification of the sulphonated oil and extraction with petrolic ether is recommended to avoid losses by the double drying in the oven.

Ash.—The ash test may be made as suggested in the Provisional Method, but is of little value as oils finished with fixed alkali will show high ash test and those finished with ammonia will show a low figure. It is therefore not even possible to form any con-

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clusion from this test for the quality of the oil, as for instance an oil finished with ammonia may contain a considerable amount of ammonium sulphate which would be entirely lost by ignition but is by no means a desirable constituent, quite the same as sodium- or potassium-sulphates would be though all of them are unavoidable constituents of every sulphonated oil.

If in the washing of the oil in the manufacturing process NaCl has been used instead of Na_2SO_4, chlorides may also be present and again the chloride of ammonia would be lost in the ash test. The only conclusion that can be made from the ash test is that the oil is neutralized with a fixed alkali if the ash is high and with ammonia if it is low. Fe_2O_3, $PbSO_4$ and other impurities could also be found in the ash.

As many oils are finished with both fixed alkali and ammonia, a reliable conclusion can only be made if both ingredients are determined.

Na_2O, K_2O and NH_3.—The amount of total alkali that is combined with sulpho-fatty acids, fatty acids and mineral acids is found by extracting in a separator 10 grams sulphonated oil dissolved in 150 cc. sulphuric ether four times with 10 cc. diluted sulphuric acid (1 : 5).

For the determination of NH_3 the acid water is rinsed into a Kjeldahl flask and the NH_3 distilled off after adding an excess of strong potash lye, and collected in a beaker filled with about 300 cc. distilled water and 10 cc. N/1 H_2SO_4. By titration the amount of NH_3 is determined.

For the determination of Na_2O or K_2O the acid water is evaporated in a platinum or silica dish (Vitreosil). In order to avoid the vapors of H_2SO_4 it may be neutralized with NH_3 before evaporating. When dry the heat is carefully raised, to avoid losses, until red hot, then cooled and weighed. The Na_2SO_4 which usually contains a little Fe_2O_3 (indicated by a reddish brown color) is dissolved in diluted HCl, a little ammonia added and the Fe_2O_3 determined as usual. After deduction of the weight of the Fe_2O_3 the Na_2O is calculated from the Na_2SO_4 found.

If Na and K both are present their amount may be calculated by determining the amount of SO_3 in the sulphates.

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NaCl.—If in the manufacture of the oil NaCl is used, the finished oil will contain some of it. The Cl is determined by washing in a separator 10 cc. of the oil dissolved in 150 cc. sulphuric ether four times with a concentrated Glaubersalt solution that is free from chlorine or chlorides. The combined salt solutions are diluted and Cl determined by titration with standard $AgNO_3$ solution.

Neutral Oil.—Ten grams of sulphonated oil or if very little neutral oil is to be expected as in Turkey red oils, 20-30 grams of the sample are dissolved in 50 cc. water in a 500 cc. separator, 20 cc. ammonia and 30 cc. glycerine are added and after the solution of the oil is perfected by slight rotation 150 cc. sulphuric ether and 15 cc. alcohol are added and the funnel vigorously shaken till a good foaming emulsion results. Through the addition of the 15 cc. alcohol the separation will soon start and will be completed in two or three hours while without the addition of alcohol it takes 24 hours or more before the separation is complete. For the second and third extraction with 100 cc. sulphuric ether for each, the separation requires usually not more than 30 to 50 minutes. The combined ether extracts are washed with 20 cc. water then with 20 cc. diluted hydrochloric acid (1 : 10) and again twice with 10 to 20 cc. water.

The first washing takes out the main part of the soap that was taken up by the ether, the washing with diluted HCl decomposes the small amount of soap left in the ether and effects a complete separation without leaving any middle layer, while the two following washings with water remove HCl from the ether, the last trace of HCl that may be left in it will be driven off when heating the ether extract in the oven. The small amount of fatty acids in the ether extract is found by titration, its weight calculated (as molecular weight may be taken that of oleic acid (282) without appreciable error) and deducted from the weight found for the ether extract.

When washing with water only, the soap is dissociated and a certain amount of fatty acids remains in the ether; a middle layer causes much annoyance. In order to avoid the washing with water I have tried the following way. I have evaporated the ether without washing it. The oil was then taken up with

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petrolic ether and 25 cc. water, 15 cc. alcohol and 10 cc. ½N alcoholic potash lye were added and all transferred into a separator. After shaking and settling the alcoholic layer was drawn off and extracted twice with petrolic ether, the petrolic ether extracts combined and washed several times with 50 per cent. alcohol. But even here the neutral oil contained still some fatty acids and a middle layer caused much trouble. For this reason this method was abandoned and the washing with water and HCl as the quicker way was adopted instead.

At the conclusion a few words about the valuation of a sulphonated oil may be in place. It need not be mentioned that everybody is inclined to prefer a bright, clear oil to a product that is cloudy or shows any precipitate of a white mass like stearic acid, or separation of water. Unfortunately the clearness of a sulphonated oil is not always an indication of its purity or good quality as oils containing a certain amount of mineral oil are usually less liable to show any separation. It seems that the combination with mineral oil makes a better solvent for the white precipitate that is so often observed in sulphonated cod oils and neatsfoot oils. The white precipitate which usually disappears when the oil is heated a little may consist of stearic acid, oxy-stearic acid and similar compounds as well as the soda soaps of these fatty acids. When the precipitate consists of those acids and their soda soaps it usually will dissolve completely in water, especially when some ammonia is added. In this case the precipitate will not be detrimental in the effect on leather.

Much worse are white precipitates that consist of lime soap or lime and iron soap which originate from lime and iron that is contained in the water which was used in the manufacture of the oil. We know that sulphonated oils have to a certain extent the capacity to dissolve lime soap or in other words, that their solution does not become cloudy when the water contains a limited amount of lime. As the ability of sulphonated oils to dissolve lime soap is rather limited, it certainly cannot dissolve any more of it if the oil already shows a precipitate of lime soap.

The cloudiness of an oil usually shows incipient separation of water or rather of glauber-salt solution. Most oils which in the beginning were clear show this cloudiness after some time

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and become clear again after a certain amount of salt water has separated. Though this separation is not desirable, it seems to be perfectly harmless to use such an oil on leather as we know very well that it is practically impossible to make a sulphonated oil which does not contain sulphates of some alkali.

The higher the amount of SO_3 combined with fatty acids or the amount of sulpho-fatty acids, the easier the oil dissolves in water, the greater is its penetrating power, the higher its carrying capacity for other oils. The latter is decreased by a high amount of neutral oil and salt, which is mostly present in the form of sodium or ammonium sulphate. The lower the figure indicating SO_3 in salts the better for the oil. But we must keep in mind that no sulphonated oil process is in such perfection that a sulphonated oil could be made that does not contain any of it.

The same applies to the neutral oil. Even the best sulphonated castor oil (which is as we all know the best oil for sulphonation on account of its alcoholic groups in the molecule) will contain a little neutral oil.

These three items (sulpho-fatty acids, neutral oil, SO_3 in salts) together with the amount of total fatty matter, unsaponifiable and water indicate best the value of a sulphonated oil, but no judgment should be passed from one or two of these items without knowing the others.

While the other ingredients are of minor value for the estimation of the oil, they should not entirely be overlooked as for instance ammonia soap is a good emulsifier in itself though not as valuable as the sulphonated component of the oil.

Whether an oil entirely neutralized with ammonia is better than one finished with alkali only, is a question that cannot be decided off hand. Though combinations of ammonia and fatty acids as well as sulpho-fatty acids are better emulsifiers and tend to give a clear oil more easily than those made with a fixed alkali, we must keep in mind that ammonia soaps decompose easily and will hardly remain ammonia soaps under all treatments which the leather undergoes. In the drying room for instance the ammonia soaps would lose their ammonia to a certain extent and free fatty-acids would result, while soda or potash soaps would remain unaltered. The freed fatty acids from the ammonia soap may

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have some undesirable effects which could not occur in the case of soda or potash soap. This may be a reason that most of the sulphonated oils are neutralized with both, partly with ammonia, partly with a fixed alkali.

Recently I saw in several analyses of sulphonated oils a figure given as their "Sulphonation Value." I found that this "value" was the percentage of "Sulphonated Oil" in total fatty matter. The amount of "Sulphonated Oil" was found by subtracting the amount of neutral oil from the total fatty matter. Or to take an example:

		Per cent.
	Total fatty matter	80
	Neutral oil	20
therefore:	Sulphonated oil	60
and	sulphonation value	$\frac{60 \times 100}{80} = 75\%$.

This "Sulphonation Value" was apparently invented to show the degree of sulphonation and to make a conclusion as to the quality of the oil. It would be ideal indeed if we could express by one figure the value of sulphated oils, unfortunately this "Sulphonation Value" is based upon an erroneous assumption, that is that all oily matter that is not "Neutral Oil" is "Sulphonated Oil." But this oily matter consists of

1. Sulpho-fatty acids which are the real product of sulphonation,
2. Oxidized fatty acids, the larger proportion of which are an indirect or subsequent product of sulphonation, and
3. Fatty acids which partly were present in the original oil, partly were formed from it by the action of the acid.

There is a number of more complicated compounds formed, but for technical purposes we may be satisfied to deal with the above three groups only.

The most valuable group is that of sulpho-fatty acids, the amount of which is found by multiplying the amount of combined SO_3 by 4.725 or 4.75 as mentioned before, the oxidized fatty acids are of a similar character and effect as those contained in sod oils, while the last group is of rather little value, I venture to say, even of less value than the neutral oil. From this we see

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that the fatty matter that is not neutral oil does not deserve the name of "Sulphonated Oil."

But there is still another error contained in this deduction. oleic acid is very well adapted for sulphonation and is sometimes used in admixture with other oils. Now for sulphonated oil made from oleic acid only, there would be no neutral oil present or only a very small amount. The "Sulphonation Value" of such an oil would be 100 or nearly 100 and according to the above assumption such oil would be pronounced one of the best in the market, though it may not be as highly sulphonated as one with, say 20 per cent. neutral oil. This example shows plainly that the "Sulphonation Value" has no value and should be discarded as quickly as possible, for all it is good for is to create wrong ideas in the heads of laymen.

The amount of water has nothing to do with the qualities of an oil for the tanning. Outside of water a sulphonated oil, we may say, contains two main groups of ingredients that is the water soluble part or the sulpho-fatty acids and their soaps which act as a carrier for other oils as well as for the third part, the partly oxidized oil which is carried into the leather.

It is natural that every tanner looks for a low water content of the oil as only the two other parts are of value to him, but he should not forget that without the water it would not be sulphonated oil. An oil with more water is often preferable to an oil with less, if it is not as highly sulphonated as the former.

In order to form a conclusion about the quality of an oil, if no full analysis is made, there should be determined at least the amount of total fatty matter, total SO_3, SO_3 in salts, neutral oil, mineral oil and water.

Outside of the analytical tests some practical tests will often be of great value, as for instance, the solubility of the oil in water with or without the addition of ammonia, the stability of the emulsion, the amount of different mineral oils which the oil could carry without separation, of the oil itself as well as of its emulsion, the stability of the oil in a 10 per cent. solution against weak acids and alkalies and against weak solutions of lime and magnesia salts.

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At the present time I will refrain from making any suggestions along this line but I think that this will be a good field for the present Committee on Sulphonated Oils to work upon.

Laboratory of F. S. Walton Co.

August, 1915.

WHAT LOOSENS THE HAIR IN LIMING HIDES?—AN UNSETTLED QUESTION.*

By Hugh Garner Bennett, M. Sc., F. C. A.

Some readers of the *Reporter* will no doubt wonder why the above question should be described as unsettled. If asked what loosens the hair in liming, they would without hesitation answer "the lime, of course." Others who have dipped into theory to some extent, and have considered the conditions of the sweating process, in which no lime has been employed will answer with equal confidence that the hair is loosened by bacteria (*i. e.*, living organism) in both these processes, and that in liming the lime merely limits and controls this action of the microbes, and that in sweating this control and limitation is—less perfectly—carried out by the ammonia which is invariably present in the sweat-pit.

Which of these views is correct? Is hair loosened by the chemical action pure and simple of the alkalies, or by the action of living organisms? No perfectly satisfactory answer to this question has yet been given, and as the question is one of considerable practical importance it may be of interest to consider the evidence and to attempt a provisional verdict.

Prof. H. R. Procter has expressed his opinion tersely in his "Principles of Leather Manufacture"—"The parts taken by the purely chemical activity of the lime, and by the action of bacteria and bacterial ferments in the unhairing process must still be regarded as uncertain."

The hair and epidermis which are removed after liming are composed of what chemists have called *keratin,* to distinguish it from other somewhat similar substances from which it differs in certain definite respects in its chemical behavior. Now it is known that keratin is insoluble in water (though it is softened by

* *Shoe & Leather Reporter*, Sept. 23, 1915, p. 31.

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hot water), but that it dissolves in caustic potash or caustic soda with partial decomposition.

There is little doubt that caustic lime would similarly dissolve it if only solutions of a similar strength could be employed, but the strongest solution of lime that can be obtained only contains 0.13 per cent. of that substance, and this is insufficient to dissolve keratin unless heat is also employed and a much longer time is given than in the case of soda or potash. Nevertheless the advocates of the theory of chemical action point out that this chemical action of lime must be present to some extent and contribute to the loosening of the hair. They also point out that it is not so much a question of dissolving keratin generally, as dissolving the softer forms of this substance which are found at the hair roots and under the horny layer which forms the outside covering of the skin.

Keratin is rightly said to be a name covering several substances of the same class, which are soluble in lime to different extents. Now the chemical action of lime in this sense can scarcely be denied, but it may be seriously questioned whether its extent is such that it contributes appreciably to loosening the hair in the ordinary liming process. The limited solubility of lime, the low temperature, the limited time, all indicate that the solvent action of the lime cannot possibly be great enough to account for the unhairing. It may be asked why this should not be settled definitely by experiments on scientific lines. What is to hinder the chemists trying the action of lime on fresh hide in the absence of bacteria, and *vice versa*? The answer is that many chemists have attempted to do this without success. It is almost impossible to obtain a piece of fresh hide which is perfectly sterile, *i. e.*, which is perfectly free from the presence and effects of bacteria. Prof. von Schroeder attempted such an experiment, and concluded that the chemical action of lime was the chief cause of unhairing, but his results have been shown to be inconclusive. Nevertheless many experiments have been made which throw light upon the question.

Many tanners have observed that if strong antiseptics are used in the soaks to prevent putrefaction, they also make their influence felt in the limes and prevent also the unhairing being carried

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out in the ordinary time employed. If lime liquors are made very nearly sterile with antiseptics, hides may be kept in them very much longer than usual without unhairing, especially if the lime liquors and hides are clean and fresh. This would seem to indicate that bacterial action is at any rate the greater influence, but does not settle the question as to whether the lime has any action in this direction as well. In such a case the liquors are exposed to the air and not completely sterile, and eventually the hides will always unhair.

A very careful experiment was once carried out by an English chemist with a calfskin. The calf was cleansed as far as possible, and his skin sterilized outside before his death. He was slaughtered at once and the skin placed immediately in a sterilizing liquor and then into a sterile, clean, fresh lime liquor and the whole was hermetically sealed for 6 months. At the end of this time the vessel was opened and the hair was found to be perfectly tight in every part. The skin unhaired freely, however, 2 or 3 days after the liquor was exposed to air. I am not aware that this experiment was published, but I have been informed that the experimenter was Dr. Parker. It is an interesting and valuable experiment, and if it can be repeated and confirmed by other workers would almost settle the question at issue. If hair is not loosened by 6 months' chemical action of lime, then the part played by this action in the ordinary process of liming is infinitesimal.

This conclusion is supported by the experiments of other workers. Procter records that "a perfectly fresh and sterilized calfskin which was not unhaired after 10 days' liming in sterilized lime liquor, unhaired rapidly on the addition of a bacterial culture to the lime." This experiment also indicates that bacterial action is the chief cause of unhairing.

An analogy may be also drawn from the Payne and Pullman system of liming in which the hides are inserted into a 1 per cent. solution of caustic soda. The alkalinity of the solution is nearly ten times that of a lime liquor, but no unhairing effect is observed. The conclusion must be that the much weaker lime solution can have very little solvent effect as an alkali.

The analogy from the sweating process is less convincing. In

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this case the alkali is ammonia and the unhairing power of ammonia has never been satisfactorily tackled. It is usually supposed to increase the unhairing effect in lime liquors, but in the writer's opinion this conclusion is very doubtful, for in all the liquors examined by him the more ammonia was present, the more plentiful were bacteria also. Procter in speaking of the sweating process, on the other hand, "has found that ammoniacal vapors alone very speedily produce this (unhairing) effect." He gives no details, however, to show that the goods and the atmosphere were sterile in these experiments, and it would be even more difficult to insure this than in the case of lime liquors.

The case of lime liquors containing sulphides is of course excluded from this discussion, for to that case the joint chemical action of the hydrates and sulphydrates in dissolving keratins is well known and understood. It may be of some interest to point out, however, that the action of alkalies on keratinous matters invariably produces some alkali sulphide, the sulphur coming from the keratin itself. Once formed its solvent effects will doubtless follow. Whether any sulphydrate of lime is formed during a sterile liming of a fortnight would be interesting and useful evidence on the point of issue. Keratin contains up to 5 per cent. of sulphur, some of which is very loosely combined, as it may be liberated as sulphureted hydrogen by the action of boiling water.

There is another point which deserves consideration in settling this question, *viz.*, the action of the lime not in dissolving the keratins, but in softening them. Hot water alone will soften keratinous matters; the effect of a hot bath on finger and toe nails is a familiar illustration. Cold water softens to a less extent, but this extent is increased by the presence of alkalies, including lime. If keratin be thus softened, it is possible that it will be much more vulnerable to the attack of bacteria. Hence it may be argued that the chemical action of lime is in this way a vital part of the liming process. In the writer's opinion this is very probable.

The action of bacteria is not always direct, but is very frequently due to the "enzymes" which they secrete. The question in consequence arises as to whether the so-called bacterial action is really the direct action of a living organism or the chemical

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action of the enzyme it supplies. This also is an unsettled question, but the tendency of modern researches is to find more and more that cases of apparent organic action are really cases of enzyme action. Indeed, attempts have already been made to isolate and utilize the enzyme of the lime liquor bacteria. There is little doubt that these attempts will ultimately succeed.

In conclusion, the writer will perhaps be expected to give his own opinion as to what is the correct answer to the question discussed above. Some idea of this may have been gathered during the discussion. In liming hides the hair is loosened almost entirely by the chemical action of enzymes which are supplied by the bacteria thriving in lime liquors. These enzymes dissolve the softer keratins and hair roots. This enzyme action is probably assisted to some extent by the chemical action of lime, not so much by its solvent effects, which is extremely small, as by its softening effects which facilitates the enzyme action. If the keratinous matters yield any sulphur to the liquor, sulphydrate of lime will be formed, which will cause a very slight but direct chemical solvent effect. The organic matter on which the bacteria feed is obtained from the gelatinous and albuminous matters of the hide.

ORIENTAL MANUFACTURE OF GAMBIER.*

By Alexander T. Hough.

In determining to get reliable information about the manufacture of gambier, I set myself a task which bristled with difficulty. Several Malays were to be found who had worked on gambier plantations, and each one, more or less, contradicted the others in his descriptions of the work. It is useless to expect a Malay to describe anything correctly, and the usual procedure when searching for knowledge is to get as many data as possible, and then sift out the concordant points, rejecting the rest as possible but improbable.

There was so little concordance in the information I gleaned regarding the manufacture of gambier that I determined, finally, to get knowledge first hand in a factory. The question arose as

* *Leather Trades' Review*, Sept. 8, 1915, pp. 512-14.

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to the locality of the nearest plantation and the best way to get there. Perseverance and cross-questioning brought out the facts that all the gambier plantations in the Pontianak district were more or less difficult of access to a European, being far in the interior, and never on the principal rivers.

Having decided that the nearest plantation was at Sungei Setai (River Setai), about 50 miles from my residence, I hired a motor boat, with Malay chauffeur and Malay guide, and set out at 5 o'clock one morning. After 3 hours' run up the principal rivers we turned off into Sungei Setai, a small river about 30 feet wide, festooned with creepers and overhung with tropical trees. It was necessary to travel at half speed as the river was full of obstructions, and several times we had to cut our way through fallen trees which completely bridged the river. After running up this river for 1½ hours we came to a Dyak village, where we were informed that it was impossible to go further in our motor boat as the river was too small and obstructed, and that it would be necessary to get to this village at 6 A. M. if anything useful was to be done, so we returned home, disappointed with the day's work.

A week later we set out again at 1 A. M., traveling by moonlight, and reached the Dyak village at 6.30 A. M. Here we engaged three paddlers and a leaky sampan (Malay canoe) to complete the voyage, which took about 4 hours, but was attended with some little excitement. A poisonous yellow and black-ringed water snake attacked the canoe and nearly succeeded in entering; we also passed several crocodiles, including a sacred white species.

Having landed at about 11 A. M., we made for the nearest factory and plantation, which was about 4 miles away. Arriving there, we were disappointed to find that the factory had not been working for some weeks, but by good fortune met a Malay who offered to conduct us to a working factory, so we started off at once, and after about 1½ hours' walking under the tropical sun reached our goal. Here I was fortunate enough to be able to watch the process from beginning to end, and to get a series of unique photographs.

The plantation was situated on a large hill, and in this case consisted of gambier and rubber interspersed, although many

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plantations are of gambier and pepper. The seed is planted when new trees are required, and the longevity of the plant is about 15 years, but it takes 3 years for them to become sufficiently big to yield mature leaves, so that the trees are worked for about 12 years. Doubtless they would yield better and for longer periods if they were properly pruned instead of being allowed to grow in a semi-wild state. The flower is of a beautiful pink and yellow color, and is spherical in form, consisting of spines radiating from a common center.

The trees grow to a height of about 10 feet. The principal branches are never cut, but only the side, or secondary, shoots. These are cut until the tree is almost stripped of leaves, and in the cutting the Chinese coolie uses a triangular *pisau dammar,* or dammar knife, which is very heavy and thick on the back and top edges, and very broad, so that he can get a good grip on the blade and bring the weight of the knife to bear on the branches in cutting. The branches are cut about 15 to 20 inches long, and as each bunch is collected it is placed and held between the knees until it becomes too large, when it is tied round with a cord. Two such bunches are brought into the factory at once and chopped up into pieces about 5 inches long, which are then ready for boiling.

The boiler consists of a circular iron pan, about 5 feet wide and 2 feet deep, which is let into the ground until its edge projects by only an inch or two. On to this edge is cemented the bottomless half of a wooden vat which just fits on to the edge of the iron pan and forms a sort of extension of it above ground. Deeper iron pans are unobtainable there, so the shallow pans are built up in this way so that the liquor shall not froth over. Any leak in the cement joint between the wooden vat and iron pan is soon filled up with the liquor and fine leaf, which dries in. Under the pan, which is let into the ground, is the furnace, caved out of the earth and built up with clay and stone, with a heat and smoke vent in the floor just behind the pan and inside the factory. The utility of this will be seen presently. A great heat is obtained in this primitive furnace, using logs of mangrove wood as fuel.

The fresh gambier leaves never have fresh water over them. The cuttings are boiled twice, and the liquor from the second

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boiling is put over the fresh cuttings. These are forked into the pan with a three-pronged instrument, about 25 gallons of second liquor are added, and the whole is then boiled for about 10 hours. When boiling commences, an instrument is suspended in the liquor from a hook, consisting of concentric circles of rattan on a bamboo frame, with three perpendicular twisted rattans for suspension. Through the middle of this is a stick, to the end of which is attached a hollow cocoanut shell with a hole about 2 inches in diameter in the top. The rattan rings are suspended just under the surface of the liquid, and the hollow cocoanut projects through the center circle about 6 inches below. The object of the rattan rings is to prevent excessive frothing, as the froth rises it breaks up on the rings, and the purpose of the hollow shell is to catch the sand, earthy matter and finely suspended leaf; for as the liquor in ebullition roughly follows the course of the convection current of heated water, it rises up the sides of the pan, goes to the center and falls, carrying with it the small particles by entrainment. From time to time the shell is pulled out and emptied into a trough above the pan. The trough consists of half the hollowed-out trunk of a tree, or an old sampan (canoe) with the nose cut off. All droppings from this flow into another small square trough underneath, and from thence into the vat containing the water for the second boiling of the leaves. During boiling the liquor is stirred with a four-pronged wooden plunger.

As the boiling nears its end the rattan rings are lifted out and the cook dips the liquor out and pours it back in a thin stream by the viscosity of which he can tell whether the liquor is sufficiently concentrated. Having decided that it is done, the fire is drawn and the leaves in the pan are forked out with the three-pronged wooden fork into the trough above and the remainder of the leaves fished out with a large rattan strainer. Having thus separated the leaf from the liquor, the latter is dipped out by means of a dipper made from a piece of tinned iron twisted into a cone and nailed to a wooden handle.

A small, finely-meshed strainer of plaited rattan is held over small tubs and the liquor is dipped out of the pan and strained into the tubs. Each tub is 14 inches in diameter by 7 inches deep,

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and holds about 3 gallons of liquor; six of these tubs are filled at each boiling, and, according to the Chinese foreman, the 18 gallons of liquor yield about 70 catties, or 88 pounds of gambier, although from the concentration of the liquor I should say the yield was much less.

To each tub of gambier is now added one catty (1¼ pounds) of *dada* or rice meal. In separating the rice grain from the husk the *padi* is beaten in a wooden mortar with a wooden pestle, and the resulting material can be separated into three parts. There is the rice grain, the husk or bran, and those portions of both which have been reduced to powder; this latter a fine brown powder, is the *dada*, which is added to the gambier liquor.

It is commonly thought that sago is added to the gambier liquor to adulterate, but this is not the object of adding the rice dust to cube gambier. It would obviously be difficult to make a dry product in an open pan without burning it, and rice dust is added to overcome the difficulty. The starch granules swell in the hot liquor and absorb the moisture, causing the whole to set to a stiff paste when cool, which may be cut into cubes and easily dried. There is, perhaps, some peculiar difficulty about drying gambier liquors, or why is the Indragiri gambier, which is manufactured in Sumatra under European supervision, exported in the pasty and not the dry form? It is improbable that sago is ever used in gambier manufacture, as rice dust is cheaper and in a more suitable form, being finely powdered; it is otherwise only used as pig food, and can be bought for 3½ gulden per picul, or about 4s. per hundredweight.

After the addition of the rice dust to the liquors they are allowed to cool, and, while still warm, a short round stick is placed in the tub, and the mixture is rubbed by hand up and down this stick for about 5 minutes. The object of doing this is obscure if it is not to make sure that there are no lumpy aggregates of rice dust, and that the mixture is thorough. On being questioned, the Chinese foreman said that the gambier would not dry if this was not done, but such a statement seems absurd.

Having become cool and pasty, the six tubs of gambier are poured into a bottomless box which fits over a perforated rabbeted board. The perforated bottom is covered with sacking and the

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sides are fitted over the rabbet, when the gambier is poured on. A considerable amount of tannin filters through into the hole in the ground underneath the box and is lost, as no attempt is made to use it, and, having lost its more liquid contents in this way, the block becomes firm, and consists of the coagulated rice-dust, crystallized catechin, and as much soluble tannin in solution as it can hold, excess of which has filtered through and been lost.

The sides of the box are now lifted off the block of gambier, which is cut into six smaller blocks with string. A board is placed against the six square faces of the front edge, and the whole block is tipped up on this edge, which now becomes the base, and each of the smaller blocks is removed and cut into cubes about 1½ inches square with an ordinary knife, which are then laid out on bamboo frames. They are dried for two days in the sun, and finally placed on the beams in the roof of the factory, where they remain for 7 to 9 days until completely dry.

The factory is built very high; in fact, about 50 feet. This is to provide plenty of drying space in the roof, which is filled with beams on which to place the racks of gambier. It will now be understood why the heat and smoke vent of the furnace is inside the factory, as all this helps to dry the gambier quickly and prevent mould.

It will thus be seen that, although the manufacture of gambier is crudely carried out, it is ingeniously done and worthy of the Chinaman. He does not want to improve its manufacture, and in Borneo, at least, does not wish to export to Europe for several reasons. First, he is not sure that he will be paid for what he delivers; and secondly, he can sell it to the natives of the East Indies for chewing with the betel nut at a greater profit.

I gained no information as to the manufacture of block gambier, which does not seem to be prepared in the Pontianak district, but probably its manufacture is not so carefully carried out; anyhow, its adulteration is notorious. I do not pretend that the process above described is carried out in exactly this manner in all gambier factories; the contrary probably obtains, and I shall most likely have more to say on this subject in a further communication, when I intend to deal with the scientific aspect of the matter.

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I may add, finally, that the gambier districts in Dutch West Borneo are the following: Sinkawang, Melian and Mengkalo on the Kapoas River, Nabang, Banjermassin, Martapoera, Karangintan, and Moearatabalong; and that the exports of gambier from Pontianak were 163,498 kilos in 1912, 6,839 kilos in 1913, and 20,456 kilos in 1914.

The quantity exported varies between very wide limits for the reason that latterly larger quantities were sent to Holland and its other colonies, and were therefore not registered as exports. There is no tax on gambier exported.

ABSTRACTS.

Asahan Gambier. The Goenoeng Malajoe Plantation Co., have issued a pamphlet describing the valuable characteristics of gambier, and giving some information about their plantation and extract works in the neighborhood of Asahan, Sumatra. A considerable area is devoted to the cultivation of the gambier plant, and the modern apparatus employed in making the extract insures a product of great uniformity. Asahan gambier has been on the market 8 years and has won approval in European markets. The manufacture is in the hands of Europeans and the product is guaranteed to be a pure gambier extract, with no addition of rice meal or any other material.

Theory of Leather Formation. W. FAHRION. *Collegium*, 1915, 332-5. Two new tannage theories, the dehydration hypothesis of E. O. Sommerhoff (abstr. ante, p. 331) and the peptisation theory of W. Moeller (*Collegium*, 1915, 49, 193) while appearing plausible for some forms of tannage, do not suit others. Sommerhoff, abandoning the theory of hide oxidation, assumes that the chemically fixed hydration water of the hide albumen is the chief agent; on its dissociation, the oxygen reacts with the tannic acids, its hydrogen with the phlobaphenes. He gives no experimental foundation for this new theory and most of his examples are taken from photography. As to chamoisage, his theory is wholly untenable. It has been proved in practice that glycerine has no part and that the tannage is solely effected by the unsaturated fatty acids of the train oil. It is correct that these are oxidized, but it is certain that they are not in part reduced, as Sommerhoff assumes; the content of saturated acids is not increased by chamoisage, otherwise this would afford a cheap process of fat hardening. Garelli and Apostolo confirmed (1913) that a glyceride never tans and can be withdrawn from the hide by ordinary fat solvents. The author is of the opinion that Sommerhoff's theory promises very little for the other tannages.

Moeller found experimentally that phlobaphenes are easier soluble in

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tannin solutions than in pure water. If a solution of tanstuff be placed over congealed gelatine the original tannin diffuses within and the faster the more the gelatine has been "peptisized" (by boiling, for instance). Following von Weimarns, he has built up the following theory. Phlobaphenes are gels insoluble in water, but by the peptisizing influence of the original unaltered tannin, are converted into gels collodially soluble. A genuine solution does not tan. Every tanstuff must contain a peptisizer (peptisator) corresponding to tannin and a peptisized substance corresponding to the phlobaphenes. Tannage depends upon "depeptisation" of the tanstuff, the hide absorbs the peptisizer, the phlobaphene becomes insoluble and is precipitated in micro-crystals on the fiber. The hide is also partly peptisized in the preparation (liming, etc.). The author thinks it more probable that phlobaphenes are formed by a primary oxidation and a secondary dehydration rather than by simple condensation of the tannic acids. Moeller assigns the intercellular substance a prominent part in tannage and gives it the same composition as hide. Van Lier has, however, shown that this substance belongs to the mucoids. Originally slight in amount, there is no doubt it is completely removed by liming, etc. Moeller maintains that solutions of pure formaldehyde will not make leather and that aldehyde leather is better the older the solution and the more "peptisized" paraldehyde it contains. The author denies this positively; tannage may be effected with pure formaldehyde and with relatively small amounts. The leather is poor from lack of stuffing with phlobaphenes which paraldehyde cannot replace. Stiasny gave up aldehyde tannage as a support of his physical theory of tanning. In quinone tannage, the hydroquinone resulting from the action of water upon quinone, acts as the peptisizer and the quinones as the peptisized gel (Moeller). But the author has shown that an alcoholic solution of quinone also tans. The hydroquinone results here only secondarily through action of the hide. Quinone leather also lacks the stuffing up with phlobaphenes. In alum tanning the peptisation condition is assumed to be intermediate. This is derided as too involved, first a gel, then solution and finally again gel formation. Moeller (following von Weimarn) explains peptisation as the formation of a complex, quinhydron for example, and with the vegetable tanstuffs, complexes of tannins with phlobaphenes. Why should not the hide molecule be equally capable of forming complex compounds with the phlobaphenes? Moeller's objection that the peptisizer must be nearly related to the peptisized substance is an arbitrary theory and not proven. The above "peptisation" is according to the author, a chemical process nor does Moeller need to explain why the peptisized hide does not dissolve. It is no strain to assume water insoluble compounds intermediate between glue and collagen.

W. J. K.

The Biological Detection and Estimation of Tanstuffs. R. KOBERT. *Collegium*, 1915, 108-117, 154-163 (reprint), 321-330 (original). *Astringents and Their Relation to Leather Formation.*—These may be classed

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as (1) mineral salts (Al, Pb, Bi, etc.); (2) artificial organic substances, such as formaldehyde and Neradol; (3) vegetable tanstuffs characterized by (*a*) astringent tasting, (*b*) effecting a drying and shrinkage of mucous membranes, (*c*) precipitating and coagulating the contents of body cells, (*d*) giving blue or green color with iron salts, (*e*) precipitating solutions of glue, mucin or albumin, (*f*) leather formation. The coarse microscopic structure of hide need not be lost in leather. The author found this unchanged in leather 1,000 years old after extraction of the tannin with alkali. After a thorough review of the literature of the theory of tanning, and of the constitution and reactions of the tanstuffs, the author takes up his original theme, the biological experiments (made in part with Fritz Sachse, Dissert. Rostock, 1914).

Several kinds of blood were used, human (from the after-birth), sheep, guinea pig, rabbit, in 2-5 per cent. suspension. Blood corpuscles, in 1-2 per cent. suspensions were prepared by centrifuging, washing or merely settling. For the regular tests, test tubes were used each containing 5 cc. blood suspension together with 5 cc. of a mixture of tannin solution with physiological NaCl solution. The observations were made after 24 hours' standing, although with the larger amounts a visible reaction often ensued in a few minutes. The only results here discussed are those with the serum-free, red blood corpuscles. If tanning is really an absorption, the enormous surface offered by the blood corpuscles should abstract the tannin from the surrounding liquid and this was the fact. On using sufficient tannin for action (without excess) this practically disappears from the intervening liquid. The blood completely precipitates in gummy form, the process being a true "agglutination" (Arrhenius). The red mass could be collected on a filter, giving a colorless filtrate. The process has the precision of a chemical reaction and can be quantitatively followed. Merck's and Schering's tannin just gave a total agglutination of 1 per cent. blood corpuscles at 1:25,000 on 24 hours' standing; an old specimen failed at 1:22,000. The tannin extracted by hot alcohol from the blood remaining on the filter was found to be partially converted into gallic acid, especially with Schering's preparation. Gallic acid is wholly without agglutinating action, hence it is possible to determine the tannin content of gall-nuts by the biological method. Powdered gall-nuts were extracted with 1,000 parts boiling physiological Nacl solution and this gave a lower limit of 1:11,000 or compared with the above ratio for pure tannin a content of 44 per cent. tannin; another especially good brand gave 50 per cent. Oak bark tannin (Extr. Cort. Quercus sicc., Merck) reacted similarly to tannin but weaker, with a limit of 1:20,000. Qualitative experiments with Eutannin (a drug prepared from myrobalans), and tanstuffs from pomegranate bark, ratanhia bark and Campeche wood showed agglutination reactions resembling those with oak tannin.

Neradol, an artificial product, but having many of the properties of tannin, was of especial interest. The author thinks that his method will be of practical value in examining all new tannin substitutes; if not agglu-

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tinating, they are to be regarded with the greatest mistrust. First, the ordinary Neradol of acid reaction was tested direct without neutralization. Its action upon serum-free red blood may be classed in 5 grades of intensity, according to the concentration: (I) weakest; clear hämolysis results without precipitation or change of color; (II) a momentary total agglutination, followed by total hämolysis; (III) total agglutination of somewhat longer duration; (IV) agglutination followed (with or without partial hämolysis) by the formation of gray flocks while the liquid, if formerly red, again becomes colorless; (V) immediate formation of flocks. None of the genuine vegetable tanstuffs show the first stage. The third stage, of most interest here, seldom occurs alone but easily passes into II or IV. The lowest limit for total hämolytic action of Neradol is 1:12,500 (based on dry substance). Neradol thus resembles the saponins and sapogenins. For the valuation of Neradol as a tanning agent, the hämolytic action is of no consequence. Agglutination is the element to be considered and the limit for this is 1:2,000 while pure tannin gave 1:25,000. Neradol then would be much weaker in action than oak bark tans. Neutralized Neradol is yet more like the saponins; the limit for its hämolytic action is 1:20,000 (dry substance).

Chromalin, a special tanning material manufactured by G. Eberle & Co., Stuttgart, was found to be somewhat superior to Neradol by the biological test.

Tables showing the results obtained with some 100 vegetable drugs follow. Among the conclusions: All drugs containing tannin are easily examined by this method. Defibrinated blood containing serum may be used for qualitative tests. For quantitative tests serum-free corpuscles must be used. The limits (table) range from 1:1,000 for Eutannin to 1:30,000 for African mangrove. The reaction must doubtless be of a physico-chemical nature at the surface of the blood corpuscles. This surface corresponds to that of pelt fiber in ordinary tanning experiments. The tanstuff is first absorbed, then chemically fixed. W. J. K.

Use of Lime in the Tanning Industry. *Shoe and Leather Reporter*, Sept. 23, 1915, p. 34 ff. ANONYMOUS. A good lime has from 90 per cent. up of CaO, while a poor one may have as low as 50 per cent. or even less. Defective burning results in part of the product being unchanged limestone quite insoluble in water. Magnesium and iron oxide cause bad slaking and bad color. The solubility of lime in water is small, only ⅛ per cent. A clear solution of lime has but small depilatory action on hides, a fairly thick milky liquor being required. Only 1 per cent. of the green weight of the hides would be necessary for unhairing if the lime is pure, but 5 per cent. is ordinarily used. The lime should be slaked some hours before it is used, so as to insure complete slaking. New limes are "harsh" in their action, so some old liquor is generally used with the fresh to "mellow" it. Mellowness is due to the presence of nitrogenous matters in the liquor. The addition of sulphate of ammonia to the lime produces a somewhat similar result, but an important part of the effect

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of the old lime is the introduction of bacteria which are supposed to be a help to the depilatory action of the lime. In general, longer liming produces softer and more stretchy leather than a shorter process. When the quantity of nitrogen in the limes reaches a certain point, the liquor becomes too active in its putrefactive effect, and must be thrown away. If, however, the hides used were very foul, nitrogen may have been introduced from this source, and such nitrogen has no effect on unhairing. Plumping may be brought about either by an alkali or an acid. The maximum plumpness due to liming is reached in 8 or 9 days. The percentage of lime that hide-substance will retain is various, but always much higher than the amount soluble in water, reaching ½ per cent. on the green weight. Half of the lime may be removed from a limed hide by repeated soaking without diminishing the plumpness of the hide. When limed hides are placed in warm water, they fall, not because of resolution of the lime, but because the hide substance itself dissolves (?—Ed.). There are two opinions in regard to the cause of the unhairing effect of lime, some regarding the chemical action of the lime as the most important, while others believe that the action of bacteria is essential. The author inclines to the latter view. Hides require longer liming in winter because the growth of bacteria is retarded by cold. In Europe liming is often done by applying a lime paste to the flesh and hanging in a warm place.

Treatment of Water with Hypochlorite. JOSEPH RACE. *J. S. C. I.*, Sept. 30, pp. 931-4. At the Ottawa station it has been found that thorough mixing is an important factor in the use of hypochlorite for the purification of water. From 0.4 to 0.5 part per 1,000,000 of actual chlorine produces good results when the mixture is good. Increased turbidity usually diminishes the efficiency of the hypochlorite treatment. During the 2 years preceding the adoption of the treatment at Ottawa, the typhoid death rate was 85 per 100,000. The rate the first year after treatment commenced was 24, and the next year it had fallen to 11. Wooden tanks for holding the 1 per cent. hypochlorite solution soon decay. Concrete has been found satisfactory. Mixer blades of cast aluminum attached to a hard bronze shaft last well, as they soon become coated with a protective covering. Galvanized iron pipe of generous dimensions lasts well, if clean-out holes are provided where incrustation may be removed. Complaints in regard to alleged injurious effects of the treated water on seeds and plants have been shown to be baseless, and where injury to piping has been alleged, it has been traced to other causes.

PATENTS.

Machine for Treating Hides, Skins and Leather. U. S. Patent 1,150,532. DANIEL P. O'BRIEN, Woburn, Mass.

Leather-brushing Machine. U. S. Patent 1,151,826. CARLETON RUHE, Olean, N. Y.

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Machine for Brushing Sole-leather. U. S. Reissue 13,984. CARLETON RUHE, Olean, N. Y.

Machine for Treating Leather. U. S. Patent 1,154,341. CARLETON RUHE, Olean, N. Y.

Method of Producing Tanning Compositions from Waste Sulphite-cellulose Liquor. U. S. Patent 1,154,762. JOHANNES J. GROSS, Hamburg, Germany. The warm sulphite-cellulose liquor is treated with hydrochloric acid, sulphuric acid and potassium chromate, concentrated to 20° B., cooled, filtered and further concentrated. The claim is made that hydrochloric acid converts some of the non-tanning matters into tanning matters, and that the resulting extract has approximately twice as much "tannin" as non-tannin, instead of nearly equal quantities as is usually the case. Another claim is that the interruption of the process of concentration results in the precipitation of a larger quantity of lime, so that the final product has only 1 per cent. of ash.

Treatment of Leather for Waterproofing and Rendering it Non-slipping. U. S. Patent 1,150,047. A. MCLENNAN ROSS, Hereford, England. India rubber celluloid, resin and gum juniper in solution are used.

Toggle. British Patent 9,736. P. C. STINGEL, Boston, Mass.

Combination Tanning Process. British Patent 8,877. (Grant of patent suspended.) OTTO RÖHM, Darmstadt, Germany. Sulphonated oils or fats free from soap are used instead of egg-yolk.

Salting Hides. British Patent 8,837. J. H. YOCUM, East Orange, N. J. To 97 parts of common salt, 3 parts of sodium sulphite are added.

Leather and Fiber Composition. British Patent 13,128. E. B. COOK, Danvers, Mass. A mixture of 20 parts leather fiber, 14 parts crude rubber, 16 parts reclaimed rubber, 15 parts diatomaceous earth, 12 parts litharge, 2 parts sulphur and a little lamp-black or other coloring matter are mixed and vulcanized.

Treatment Preliminary to Tanning. British Patent 12,952. R. VIDAL, Asnieres, France. Hides and skins are cleaned, preserved, and depilated by being treated with an aqueous solution containing from 5 to 10 per cent. of a crystallized alkaline sulphite or hyposulphite associated with an alkali, ammonia, or an alkaline carbonate or sulphide. An after-treatment with acid may be employed before stripping the hair, the effect being to make the skin tougher. As an example, sheepskins are soaked for 12 to 15 hours in a solution containing 5 to 10 per cent. of an "association" of 66 per cent. of hyposulphite or crystallized sulphite with 33 per cent. of anhydrous carbonate. Before the hair is stripped, the skin may be subjected to a bath containing 5 to 10 cc. of sulphuric acid to the liter. An alternative association consists of 90 per cent. of hyposulphite or sulphite and 10 per cent. of alkaline sulphide, alkali, or 20° Bé. ammonia. The associations may be made by fusing together the crystalline ingredients or by employing concentrated solutions in the case of alkalies. The above process also cleans, bleaches, and removes the grease from the hair or wool.

Tanning Drum. U. S. Patent 1,155,866. BONA ALLEN, JR., Buford, Ga.

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A STUDY OF THE CHANGES IN SKINS DURING THEIR CONVERSION INTO LEATHER—(Continued).

By Anton A. Schlichte.

The sections showed that the flank was decidedly of a looser structure than the rest of the skin. The loose structure was noted in the very beginning of the process and the soap treatment apparently failed to remedy this defect. Even if the lime soap formed should hinder further action of the lime, it could not change the existing loose structure into a compact one. The

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EXPERIMENT S-36—CHANGES IN VOLUME.

Condition of the skin	Number I			Number II			Number III		
	Volume in cc.	Increase in cc.	Per cent. increase	Volume in cc.	Increase in cc.	Per cent. increase	Volume in cc.	Increase in cc.	Per cent. increase
Dry salted	40.9	—47.3	—53.5	45.1	—56.0	—55.3	71.5	—44.4	—38.2
In water 24 hours	72.2	—16.0	—18.1	85.4	—15.7	—15.5	106.0	—9.9	—8.6
In water 48 hours	88.2	0.0	0.0	101.1	0.0	0.0	115.9	0.0	0.0
In lime 48 hours.....	103.5	15.3	17.3	137.8	36.7	36.3	163.7	47.8	41.2
In lime 24 hours.....	119.9	31.7	35.9	137.9	36.8	36.4	184.4	68.5	59.1
In lime 72 hours.....	120.1	31.9	36.2	137.2	36.1	35.6	187	71.1	61.4
In lime 96 hours.....	120.5	32.3	36.6	146.5	45.4	44.8	194.4	78.5	67.7
In lime 120 hours.....	120.2	32.0	36.3	139.2	38.1	37.6	190.8	74.9	64.6
In lime 144 hours.....	121.9	33.7	38.2	144	42.9	42.4	180.6	64.7	55.8
In lime 168 hours.....	121.9	33.7	38.2	—	—	—	174.7	58.8	50.7
In lime 192 hours.....	—	—	—	—	—	—	175.8	59.9	51.6
Unhaired and fleshed ..	66.1	—22.1	—25.0	79.2	—21.9	—21.6	93.	—22.9	—19.8

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EXPERIMENT S-36—CHANGES IN VOLUME.—(*Continued.*)

Condition of the skin	Number IV			Number V			Number VI		
	Volume in cc.	Increase in cc.	Per cent. increase	Volume in cc.	Increase in cc.	Per cent. increase	Volume in cc.	Increase in cc.	Per cent. increase
Dry salted	43.3	—34.0	—44.0	63.1	—37.3	—37.1	70.6	—46.5	—39.6
In water 24 hours.....	69.8	—7.5	—9.7	96.3	—4.1	—4.1	113.0	—4.1	—3.5
In water 48 hours.....	77.3	0.0	0.0	100.4	0.0	0.0	117.1	0.0	0.0
In lime 24 hours.....	177.8	46.5	52.4	148.5	48.1	47.9	193.9	76.8	65.5
In lime 48 hours.....	122.1	44.8	58.0	162.7	62.3	62.0	202.9	85.8	73.2
In lime 72 hours.....	126.3	49.0	63.5	173.9	73.5	73.1	208.9	91.8	78.3
In lime 96 hours.....	126.6	49.3	63.8	179.3	78.9	78.5	220.0	102.9	87.7
In lime 120 hours.....	132.4	55.1	71.4	181.1	80.7	80.3	212.6	95.5	81.5
In lime 144 hours.....	122.4	45.1	58.4	161.1	60.7	60.4	183.1	66.0	56.3
In lime 168 hours.....	125.7	48.4	62.5	177.0	76.6	76.3	196.7	79.6	68.0
In lime 192 hours.....	—	—	—	—	—	—	172.7	55.6	47.5
Unhaired and fleshed ..	61.0	—16.3	—21.1	78.3	—22.1	—22.0	100.8	—16.3	—13.9

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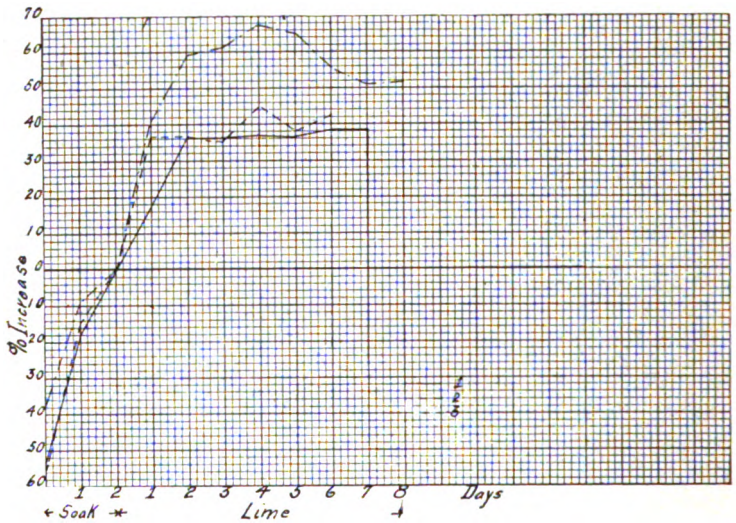
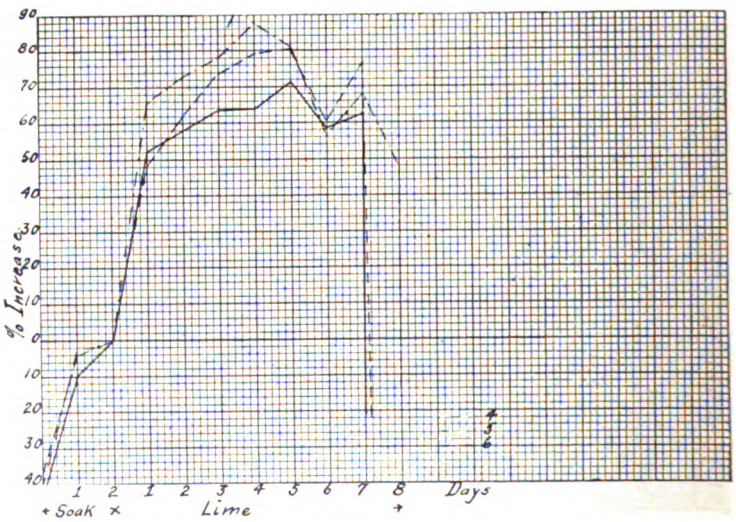
EXPERIMENT 36.—VOLUME.

Per cent. increase on 48-hour soaked volume.



EXPERIMENT 36.—VOLUME.

Per cent. increase on 48-hour soaked volume.



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samples were all unhaired, fleshed, bated, pickled and chrome tanned and pronounced fair leather. The grain in all samples was good and showed that the soap treatment caused no apparent harm. The volume measurements are given in table, Experiment S-36, and are shown also in curves.

Some attempts were made to fill the flank so that it would be as full as the rest of the skin. The hides after depilation were suspended in 1, 2, 5 and 10 per cent. solutions of glue and a few cubic centimeters of methylene blue were added. The dye showed the extent of penetration of the solution. After the usual chrome tannage, the results obtained were unsatisfactory. Some flanks appeared to have been improved and others were as if they had not been treated with glue. Then 1, 2, 5 and 10 per cent. gelatine solutions were tried. The results were practically the same as before. In both cases the finishing of the leather was attended by difficulties. Some pieces took too great a gloss and others remained too dull. In the next series fresh blood and glue, blood and gelatine were used. About 50 per cent. of blood and 50 per cent. of a 10 per cent. solution of glue or gelatine were used. Although great care was taken to watch the hides carefully, many were destroyed by bacteria. Even the addition of germicides, such as mercuric chloride and phenol failed to take care of the putrefactive bacteria. So long as bacterial limes are used this process will be attended with very great difficulties and can hardly be made commercial.

Some experiments were tried on pickled stock using glue and gelatine to fill the flanks. The results did not justify the continuation of work along these lines.

The greatest dfficulty in experiments of this kind is that the judgment of an expert is required to determine improvements. Moreover, improvements of a commercial value must be noticeable not only to an expert but also to the layman.

Results of Studies of Changes in Weight, Volume and Area of Calfskin During the Tanning Process.

The results of these tests can best be studied from the curves which are computed to a common basis of percentage change from the condition existing when the skin entered the limes.

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Measurements of change in superficial area were made in Experiments 26 and 28 and are given in detail in the tables.

The dry salted skins expanded 27.1 and 19.4 per cent. respectively in area during the soaking process but both remained relatively constant in area throughout the subsequent operations of liming, bating and pickling. No. 28 showed a considerable increase after unhairing but this mechanical stretching disappeared in the pickle. Through an oversight the area of the wet tanned skin was not determined in Experiment 26 and the area for the dried finished leather while about 5 per cent. greater than that of the dry salted skin, has little significance on account of the impossibility of standardizing the amount of stretching the leather received in the drying process. The leather of S-28 measured wet showed a shrinkage in area of about 10 per cent. compared with the pickled stock and an increase in area of about 12 per cent. compared with the dry skin.

A comparison of the weight and volume curves of all experiments shows great general similarity. Both volume and weight increase in approximately the same ratio during the soaking and liming process. The increase is rapid during the first 24 hours in water and slower after that time. On putting into lime the increase is again very rapid during the first 24 hours and becomes slower thereafter, reaching a maximum after about 5 days in lime. These limes were all bacterial but did not contain added sulphides.

The increase in volume of different pieces varies from 40 to 80 per cent. The experiments on change in area quoted above show that very little change took place after the skin was soaked. These changes in volume are therefore an almost direct measurement of change in thickness. This increase in volume and hence approximately of thickness runs up to a maximum of 90 per cent. over that of the soaked hide. The least total increase in volume shown by any skin is 38 per cent. over that of the soaked hide.

Marked differences exist between different portions of the same skin limed in the same solution. In each Experiment 25, 36 and 39 a half calfskin was trimmed and cut at right angles to the backbone into three pieces of approximately equal size. These three pieces were carried through the whole operation together.

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The differences in the maximum amount of swelling of these three skins during the liming process is as follows:

	Shoulder Per cent.	Middle Per cent.	Rump Per cent.
Experiment 25.....	51	40	62
Experiment 36.....	72	80	88
Experiment 39.....	70	90	65

No conclusions can be drawn except that different portions of a dry salted skin may swell very differently in the limes. This may be due to differences in thickness, in structure, in amount of fat or to other causes and is discussed somewhat later.

While the curves show that the changes in volume and weight are in general similar, the exact relationship is shown in a very similar manner by the curves of density. Tests 25, 26, 27, 28 and 39 are available for a study of this relationship. Any errors of measurement are magnified in this method of treatment and as is to be expected the curves are not altogether consistent. Certain general features are, however, clearly recognizable. The density decreases on soaking in water, but usually increases or stays constant during the first 24 hours in limes. It then decreases as the liming process proceeds and reaches a maximum after 96 hours in the limes. It then rises to a distinct maximum after 144 hours in lime but usually falls again within the next day or two. The density falls again in the bating process whether a bran drench or lactic acid be used and rises sharply in the pickle to fall again somewhat in the wet tanned leather.

The changes are in general those which would be expected when a material heavier than water absorbs water and swells. The volume increases more rapidly than the weight. The same phenomenon persists in the limes. The sharp change in the curve while still in the limes is unexpected but may be in some way connected with bacterial action. The immersion in the feebly acid bath swells the hide more rapidly than the weight increases and hence the density falls again. The pickle shrinks the skin and brings its density back to a figure nearly that of the dry skin.

The most noticeable defect in calfskins is the flabbiness of the flank. Microscopic examination showed this part of the skin to be of loose structure and thinner than the rest. The relative swelling of butt and flank was tested in Experiments 29, 33 and

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39B. In every case the flank swelled more than the butt, the figures for maximum increase in volume on 24 hours soaking over the dry volume being:

	Butt Per cent.	Flank Per cent.
Experiment 33	25	45
Experiment 39B	61	86

The maximum swelling in lime referred to the volume after soaking 48 hours was:

	Butt Per cent.	Flank Per cent.
Experiment 29	63	92
Experiment 39B	60	71

The effect of coating the flesh side of a calfskin with lime soap at the time of its immersion in the limes is shown in the table and the two sets of curves in Experiment 36. The soaped pieces all swelled decidedly more than the unsoaped. The maximum swelling expressed in percentage increase on the wet volume is as follows:

	Not soaped	Soaped
Shoulder	38	72
Middle	45	81
Rump	68	88

The volumes of the soaped pieces decrease more after unhairing and fleshing than do those of the unsoaped, so that the effect of the soap seems to be lost. Volume measurements were discontinued after this point and therefore quantitative figures on the finished leather are not available. However, the pieces which had been soaped before liming seemed slightly fuller.

Study of Depilation in Sterile Limes—Review of Literature.

Although the bacteria of bating and puering have been studied quite thoroughly, those of the limes have been more neglected. While certain agents have been known for some time, which without the aid of bacteria, were able to depilate a hide, still in the ordinary processes used in practice, the presence of bacteria was not only taken for granted, but if through any reason bacteria were absent active cultures were always added. This idea has had so firm a hold that, whenever a new tannery was

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established some old lime from another tannery was conveyed to the new lime pits in order to "start," that is inoculate them.

The idea that a solution of lime could, under sterile conditions, cause loosening of the hair so that a hide could be unhaired easily, was considered impracticable. Parker[13] states, "Formerly it was believed that the lime swelled the fibers of the hide, dissolving the hair bulb or root and loosening the epidermis, thus rendering the removal of the hair easy; but the liming process is now known to be both chemical and physical, the loosening of the hair being largely due to the action of enzymes and the products of bacteriological action. Hides cannot be unhaired by sterile limes, so that the process of Payne and Pullman,[14] by which the hides were first soaked in caustic soda and afterward in calcium chloride, so as to form lime within the fibers, was unworkable unless preceded by the soaking of the hides in a foul soak to obtain the necessary bacteriological action." He also states,[15] "It was fully realized that bacteriological action played an important part in the unhairing and that the action of old limes was largely bacterial and that hides could not be unhaired from a sterilized lime." Procter[16] believed that bacteria were essential in the liming process. Stiasny[17] states that the liming process is both a chemical and bacteriological one. Villon in his "Traite de la Fabrication des cuirs" discusses the liming and sweating processes. He states positively[18] "L'echauffe est une fermentation particuliere causee par un microbe determine. L'epilage a la chaux est cause par la meme fermentation. Que la peau ne se depile pas en presence de la chaux apres sterilization." He states that the unhairing of skins is due to the action of definite bacteria and that sterilized lime will not cause unhairing of a hide. He sterilized his samples of hide by means of dry heat. He subjected the samples to 50° C. for 24 hours and then 110° C. for 10 minutes. Schmitz-Dumont[19] has shown that not all the bacteria present were killed by this treatment.

[13] *Jour. Soc. Chem. Ind.* Vol. 29, p. 912 (1910).
[14] English patent, No. 2,873.
[15] *Jour. Soc. Chem. Ind.* Vol. 31, p. 371 (1912).
[16] *Prin. of Leather Mfg.* pp. 135, 137.
[17] *Leather Trades Rev.* July 2, 1913.
[18] *Villon Traite de la Fabrication des cuirs*, p. 487.
[19] *Ding. Polyt. Jour.* Vol. 300, p. 140.

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Von Schroeder[20] made many experiments along the above lines, and as his conclusions are different, his work will be given more fully. His methods were as follows: Hides were obtained from a tannery, washed 3 days in water, then placed in a saturated salt solution. The salt solution was changed until the hide no longer absorbed salt. The hides were kept in this salt solution and were considered sterile. The lime used was sterilized in the following manner: The lime solutions were placed in flasks around the neck of which cotton moistened with salicylic acid had been wound so that the whole could be covered with a Petri dish. These flasks were placed in a water bath up to 1 inch from the top of the neck in water. The bath was then heated to boiling and kept boiling ½ hour. This treatment was repeated on 3 successive days. This lime solution, was then called sterile. In order to observe the action of sterile water on hides, several flasks of water were treated precisely like the lime solutions. The sterile hides were placed in the sterile lime and sterile water flasks June 29th. On July 4th, a sample was taken from a water and a lime flask. No odor was perceptible in either case. The hair could be removed with great difficulty and in fact it was almost impossible to get it off. One cubic centimeter of the water and one of the lime solution were now transplanted into 10 cc. of gelatine. All these sub-cultures gave a positive result, that is a growth of bacteria or molds, whereas if the solution had been really sterile there should have been no growths. On July 11th a flask of each kind was again opened. The hair slipped easily. Again all sub-cultures made gave positive results. On August 3rd the remaining flasks were opened and all sub-cultures again gave positive results. Moreover, the solutions all had a putrid odor.

Van Schroeder then took part of the water in the flasks, added it to some sterile limes and the sub-cultures made showed few colonies. His conclusion was that the lime killed the bacteria contained in the water. His final conclusion based on this last experiment was that in the limes, unhairing takes place without bacterial action in a short time, but that in pure (reinem) water only after bacteria have developed and produced ammonia enough to make the solution alkaline. His second series was as

[20] *Ding. Polyt. Jour.* Vol. 301, pp. 65, 90.

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follows: The hides from the saturated salt solution were placed in 99 per cent. alcohol which was renewed every day for 4 days. These hides were considered sterile. The flasks containing water and lime water solutions were sterilized as before. All except one of the sub-cultures taken after 4 days gave positive results. In this case some hairs were transplanted to gelatine by means of a forceps sterilized in a flame. There is a possibility that the forceps was too hot and killed the bacteria, or that the melted gelatine was too warm. After 6 days two more flasks were opened and sub-cultures made. All but two gave positive results. These two sub-cultures were made by transplanting 0.1 cc. and 0.01 cc. of the lime solution in 10 cc. of gelatine. The final conclusion drawn from these experiments was that "Die Vorbereitung der Haut zum Enthaaren durch den Aescher process von Bakterien überhaupt unabhangig und nur eine Wirkung der alkalischen Reaction des Kalkes ist." Von Schroeder then assumes that Villon's idea that *bacillus pilline* must be present in limes in order that the hair be loosened, is no longer true. Unfortunately Von Schroeder died before the work was completed and the paper was published by others. The results do not bear out the assumption that the hides and solution used were really sterile. On the contrary all but two sub-cultures from the supposedly sterile solutions gave positive results. The sub-cultures which were negative under aerobic condtions were not duplicated under anaerobic conditions. There is no valid reason why anaerobic bacteria could not have been present. He also neglected to guard against the inhibiting action of the lime. He showed at great length that the lime solution killed, or rather to be accurate inhibited the growth of bacteria obtained from the infected water used in the first experiment. Afterward he did not take this fact into consideration, but transplanted his solution from the lime flasks into the same amount of gelatine—10 cc. as in the experiment using water only.

Griffith[21] made several experiments on a sterile liming process using carbon bisulphide and phenol as disinfectants. He does not give any data nor information about the actual methods used or precautions taken to prevent infection of the solutions but merely speaks of "pieces of hide previously sterilized with carbon bisul-

[21] JOURNAL Amer. Leather Chem. Asso., Vol 5, p.115 (1910).

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phide and with phenol and the liming carried out in sealed jars. The carbon bisulphide hide unhaired in 24 days and the phenol hide unhaired in 18 days and an experienced bacteriologist was unable to discover the presence of bacteria. Von Schroeder experimented with fresh salted hides under sterile conditions and he was unable to discover that the absence of bacteria influenced the activity of the lime as a depilatory." The above statements would have been more convincing if the methods of bacteriological control had been given more fully. Griffith concedes that Von Schroeder's work was correct and he admits that the latter worked under sterile conditions. As was pointed out before this was not the case. Von Schroeder never had sterile conditions prevailing in any of his experiments as his sub-cultures always showed bacteria or molds. Griffith relied entirely on carbon bisulphide as a sterilizing agent. Carbon bisulphide may be an antiseptic agent but it is not a disinfectant for it does not kill all organisms, as was shown by Procter.[22]

The experiment with carbon bisulphide gave approximately the same results as that with phenol. This may have been due to the fact that under the conditions existing during the experiment the carbon bisulphide was present in sufficient quantity to prevent a noticeable increase in the number of bacteria present. The above experiments cannot be accepted as accurate in the scientific sense.

Experimental Work on Sterilization of Hides.

The following experiments were planned to settle definitely whether bacteria were necessary in the depilation process. The sterilization of hides offered the first difficulty. After reading of various methods[23] using sulphur dioxide, phenol, etc., the Seymour-Jones method was finally adopted as offering the best chances of success. The method consists of immersion of the hide for 24 hours in a 0.02 per cent. solution of mercuric chloride and a 0.5 per cent. solution of formic acid.

In order to test Seymour-Jones method of sterilization for its effectiveness as a sterilizing agent the following experiments were made. Samples of hide about 1 x 2 centimeters were soaked in

[22] Procter, Principles of Leather Manufacture, p. 135.

[23] Journal Amer. Leather Chem. Asso., Vol 5, pp. 508-10.

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the solution 24 hours. They were then removed with sterile forceps and washed three times by immersion, using a liter of sterile water each time. Then they were planted by means of sterile forceps into 150 cc. of sterile medium, beef tea, gelatine, agar, pea-bean medium, and litmus glucose gelatine being used. The results are shown in the table.

SEYMOUR-JONES TEST.

No.	Beef tea	Gelatine	Pea-bean	Agar	Anaerobic conditions. in a Novy jar, over hydrogen. Litmus glucose gelatine	Check for Anaerobes B. tetanus	Check Aerobes B. lactici
1	—	—	—	—	—	+	+ + + +
2	—	—	—	—	—	+	+ + + +
3	—	—	—	—	—	+	+ + + +

Although these solutions all showed negative results it is necessary, before admitting the test to be conclusive, to show that the amount of mercuric chloride transferred could not have been sufficient to have inhibited the growth of bacteria in the culture media. Mercuric chloride acts as an antiseptic agent even in dilutions of 1 to 100,000. The samples after washing thoroughly in 3 liters of sterile water had very little mercuric chloride adhering. Moreover, the volume of medium used was large, 150 cc. or more in all cases. This again increases the dilution of the mercuric chloride and hence eliminates its antiseptic action.

The dilution at which formic acid still exerts its antiseptic action is not known definitely. The fact was taken into consideration, however, that the antiseptic action of formic acid is usually less than that of mercuric chloride. If one assumes the piece of hide transferred, to be all formic acid, and then takes into consideration the dilution resulting from the washing in sterile water, one will see that the dilution is more than 1 to 200,000 and that there is no chance of any antiseptic action interfering with the results. In order to check whether the medium was suitable for growing bacteria, *bacillus tetanus* and *bacillus acidi lactici* were planted under anaerobic and aerobic conditions respectively. The results were positive in all cases.

Since the checks were always positive and the sub-cultures

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from the sterilized hides negative, it was therefore considered proven that the Seymour-Jones method of sterilization is effective under the given conditions of experiment.

Test for Bacteria in the Limes.

Since there might be some question as to the presence of bacteria in the limes, sub-cultures were made on agar, beef tea, pea-bean media and gelatine. All sub-cultures gave positive results.

Wood[24] has shown that bacteria of various kinds are present in the limes. Abt[25] has also proven that bacteria are present in the liming process.

The medium used in transplanting sub-cultures in all the following experiments was slightly more alkaline than that usually employed for this purpose.

Experimental Work—Laboratory Tests on Depilation.

The procedure now used was as follows: A 250 cc. Soxhlet flask, provided with a tight cotton plug was sterilized for 1 minute at 200° C. in a dry heat sterilizer. It was cooled and 175 cc. of water and 50 grams of slaked lime were added. The flask was then autoclaved at 110° C. for 20 minutes and allowed to cool. A piece of hide which had been previously sterilized in a solution (Seymour-Jones) of 1-5,000 mercuric chloride and 0.5 per cent. formic acid, for 24 hours, was added to this solution by means of sterile forceps. This flask was then examined every 2 or 3 days, great care being taken to prevent infection of its contents. After 11 days the hair could be removed with difficulty, but after 13 days the hide could be easily unhaired.

In order to prove conclusively that bacteria were absent, sub-cultures of the lime solution and of hair were made on various media under aerobic and anaerobic conditions. That the medium used was suitable for the growth of bacteria was proven by planting test organisms. For this purpose *bacillus acidi lactici* and *bacillus tetanus* were used under aerobic and anaerobic conditions, respectively. The results obtained are shown in the following table:

[24] *J. Soc. Chem. Ind.*, Vol. 29, p. 666. (1910).

[25] *Bull. Syndicat. Gen. Cuirs et Peaux*, p. 416, Nov. 10, 1908.

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CHECK TEST ON STERILITY OF CONDITIONS.

	Beef tea	Gelatine	Pea-bean	Under anaerobic conditions in a Novy jar previously exhausted and hydrogen passed in. Litmus glucose gelatine
1 loop of lime solution	—	—	—	—
Hair	—	—	—	—
Checks	+	+	+	+

These results are very satisfactory and show, since all the subcultures were negative and the checks positive, that no bacteria capable of growing were present in the limes used.

After it had been shown that the Seymour-Jones method of sterilization with mercuric chloride and formic acid was reliable and preliminary tests had shown that it was possible to unhair a skin with sterile limes, the following series of tests was undertaken to study the process more quantitatively. Four different solutions were used to determine how lime alone, and lime with sulphur compounds acted. One flask contained lime only, a second lime and red arsenic sulphide, a third, lime, red arsenic sulphide and hair, and the fourth lime and hair. The solutions containing hair were boiled vigorously for 45 minutes, before use, with the idea that some hydrolysis of the hair would take place with formation of soluble sulphur compounds and amino acids and that thus the action of an old lime might be simulated. The details of the tests are as follows:

Four pieces of dried calfskin 2 x 3 inches in area were soaked 24 hours in a solution of 0.02 per cent. mercuric chloride and 0.5 per cent. formic acid. Four 250 cc. Soxhlet flasks were plugged with cotton and sterilized for 1 minute at 200° C. in a dry heat sterilizer. To one of these flasks 50 grams of lime and 175-200 cc. of water were added. To another sterile flask 50 grams of lime, 175-200 cc. of water and 1.5 grams of red arsenic sulphide were added. Then the flasks which were to contain boiled hair were prepared as follows: 200 cc. of water, 50 grams of lime and 10-12 grams of hair clipped from a calfskin, were boiled vigorously for 45 minutes. This solution was placed in a sterile flask. Then 200 cc. of water, 50 grams of lime, 1.5 grams of red arsenic sulphide and 10-12 grams of hair were boiled 45 minutes and put into the fourth sterile flask. Then the four flasks were autoclaved for 20 minutes at 110° C. A piece of

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EXPERIMENT 38—CHANGES IN HIDES DURING DEPILATION IN STERILE SOLUTION.

	Number I	Number II	Number III	Number IV
Date	Lime, arsenic, sulphide and hide	Lime and hide	Lime, arsenic, sulphide, hair and hide	Lime, hair and hide
10–3	All the flasks charged.			
10–4	All flasks well shaken for	five minutes.		
10–5	10 gms. sterile lime added	to Numbers II and IV.		
10–10	Hair pulled easily almost all dissolved.	No noticeable change.	Hair pulled fairly easy.	No change.
10–12	Hair nearly gone.	Hair pulls but not easily.	Hair slips very easily.	Hair slips but not as well as I, better than II. No odor noticeable.
10–19	Has odor of hydrogen sulphide.	Hair slips easily. A slight odor, not hydrogen sulphide.	Odor like urine, decomposition, no hydrogen sulphide.	
10–29	No change; still hydrogen sulphide odor.	Hair slips very easily, slight odor not hydrogen sulphide.	Same.	Same.
11–5	Slight hydrogen sulphide odor. Top layer going fast; corium firm.	Upper layer firm, no odor. Hair slips very easily.	Hide beginning to disintegrate, that is, to soften so it can be torn with tweezers. Odor same, but weaker.	No odor. Upper layer easy to remove by scraping. Corium firm, however.
11–17	Same as above.	Same. No odor. Grain not soft.	Same odor; otherwise about like Number I.	Top layer going; no odor, scum like soap on flesh side.
12–1	Upper layer still present but badly decomposed.	Same; upper layer still good.	Same, not much odor, upper layer all gone.	Upper layer still present and fairly firm.
1–12	Upper layer gone very little odor.	Upper layer attacked and soft; can be scraped off. No odor.	No odor. Flesh side badly attacked. Corium good.	Upper layer soft and practically disintegrated. Corium good.
2–6	Flesh side mushy, no odor. Corium good.	No odor. Flesh side mushy. Corium good, but somewhat softer.	No odor. Flesh side badly attacked; mushy, corium good.	Upper layer gone. Corium good. No odor. Flesh side mushy.
2–12	Flesh side going. No odor corium good about same. Can be scraped off by tweezers.	About the same, no odor.	Same, no odor.	About the same. Corium good. No odor.
3–8	No odor. Very glassy almost all gone.	No odor. Flesh side very mushy. Corium softer. Still has firm feeling. Can be scraped off.	No odor. Corium very soft glassy almost all gone. Very small piece left.	No odor. Piece still left. Flesh side very mushy swollen like scum. Grain side smooth, but scrapes easily. Lower layer still very firm.

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sterile hide was now planted in each of the flasks after cooling, by means of sterile forceps.

The following table gives some of the observations made on these samples. Every time the hides were examined great care was taken to handle them with sterile instruments and in such a manner that they remained sterile. The flasks were all kept at the room temperature. They were not examined every day, for the danger of contamination would have increased at a greater rate than the notable differences in the skin. The remarks concerning the condition of the skin are rather indefinite to be sure, but the changes were very gradual and consisted in the main in such as are hard to describe accurately.

In order that there might be no question of the sterility of the various flasks, sub-cultures were made on various media after the test had been running 2 months. Gelatine, beef tea and pea-bean media were used for aerobic and litmus glucose gelatine for anaerobic experiments. *B. acidi lactici* and *B. tetanus* were used as checks respectively. The results follow in the table.

EXPERIMENT 38.—CHECK ON STERILITY OF SOLUTIONS.

Number of flask	I	II	III	IV	
Gelatine plates	—	—	—	—	Planted 2-12-14
Gelatine tubes	—	+*	—	—	Examined daily from
Pea-bean tubes	—	—	—	—	2-12 to 2-24
Beef tea tubes	—	—	—	—	
Checks	+	+	+	+	
Anaerobic conditions in Novy jar over hydrogen	—	—	—	—	
Litmus glucose gelatine					Planted 2-12-14
Checks	+	+	+	+	Examined 2-26-14

* One positive result out of eight gelatine tubes.

It will be noted that all the results are negative with the exception of one of the eight gelatine tubes planted from Flask II. To study this organism further it was transplanted and plated. It proved to be a streptococcus, white, liquefying gelatine and was probably Matschek's white streptococcus. Then six more gelatine sub-cultures were made from the original flask. All were negative. Therefore, it is reasonable to presume that this one tube became infected through air and technique. The anaerobes were transplanted to litmus glucose gelatine and placed in a Novy jar. This was exhausted to 28.8 millimeters vacuum, then hydrogen was passed in. This process was repeated three times then the jar was closed and left for 14 days. No

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growths were noticeable. Tetanus bacillus was used as a check and gave a good growth in litmus glucose gelatine to which one loopful of sterile lime water had been added. In the case of aerobes, the check used on gelatine with one loopful of sterile lime was *bacillus acidi lactici.* In all cases the effect of the lime and water which was unavoidably conveyed by the platinum loop during inoculation, and which might have had an antiseptic or germicidal action, was provided for by using a large amount of medium at least 15 cc. in each case and to be more certain, for each set one flask containing 100-150 cc. of medium was used.

This Experiment 38 was continued 5 months as shown by the table and at the end of the period, the flasks were again tested. All tubes and flasks showed negative results, that is no growths. The checks were all positive showing that conditions were favorable for the growth of bacteria. Details are given in the following table:

EXPERIMENT 38.—FINAL CHECK ON STERILITY OF SOLUTIONS.

Number of flask	I	II	III	IV	
Gelatine plates	—	—	—	—	Planted 3-8-14 examined daily from
Gelatine tubes	—	—	—	—	3-9 to 3-23
Pea-bean	—	—	—	—	
Beef tea	—	—	—	—	
Checks	+	+	+	+	
Anaerobic conditions Litmus glucose gelatine	—	—	—	—	Planted 3-8-14 Examined after 14 days
Check	+	+	+	+	

EXPERIMENT 40.

This experiment was made both to check results of the previous one and to see whether the presence of hair had any marked effect on the changes taking place during the sterile liming. The samples of hide were sterilized 24 hours in 0.02 per cent. formic acid then transferred with sterile forceps to sterile flasks containing lime, and lime and arsenic sulphide. The samples were in one case hide which had had the hair closely clipped off before sterilization and in the other case normal hides with hair on. At the same time 20 grams of hair were sterilized 3 days and then placed in 600 cc. of water containing 50 grams of lime with the idea in mind of noting changes on pure hair under said conditions. The results follow in the table. Sub-cultures were made from all flasks on various media precisely as in the previous tests. The results were all negative and are shown in the following tables:

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EXPERIMENT 40—CHANGES IN HIDES DURING DEPILATION IN STERILE SOLUTIONS.

	Number I	Number II	Number III	Number IV	Number V
	Shaved	Hair on	Shaved	Hair on	Hair
Date	5 grams lime 0.15 gram AS_2S_3 400 cc. water	Same as Number I	5 grams of lime 400 cc. water	Same as Number III	20 grams 50 grams lime 600 cc. water
12–3	Into all solutions after 24	hours sterilization in Sey-	mour-Jones solution.		Hair sterilized 3 days.
12–6	No change.	Hair slips very little when pulled strongly.	No change, no odor.	No change, no odor.	No change.
12–7	" "	Same.	No change, no odor.	" " " "	" "
12–8	" "	"	" " " "	" " " "	" "
12–9	Hair slips some, that is, comes off on scraping.	Hair slips more easily. Slight odor of hydrogen sulphide.	" " " "	Hair tight, can be pulled; slight odor.	No odor. No change.
12–13	Hair can be scraped easily. Very slight odor epidermis attacked.	Hair slips very easily; much of it dissolved. Epidermis attacked; slight hydrogen sulphide odor.	" " " "	Hair still tight, not much if any odor.	Same.
12–20	Not much odor, may be slight hydrogen sulphide. Upper layer badly attacked. Hair all gone. Corium still hard and firm.	Hair nearly all gone, upper layer mushy. Corium good, odor of hydrogen sulphide.	May be slight odor, hard to tell. Hair can be scraped easily. Corium good and harder than Numbers I and II.	Hair slips fairly easy. Corium hard like Number III. Flesh side somewhat swollen. Very little odor if any.	Slight odor of hydrogen sulphide.
1–5	Upper layer badly attacked. Corium firm and hard. Very little odor.	Not much odor of hydrogen sulphide. Upper layer more attacked than Number I. Patches of it gone.	Upper layer not soft like I and II. No odor.	Hair slips very easily. Upper layer attacked, it can be scraped off. No odor.	Same.
1–8	About same. No odor, same. Upper layer very mushy. No odor corium firm. Flesh side swollen.	About same. No odor, same. Upper layer almost all gone. No odor. Corium good. Not so firm.	Same. Corium firm, same. No odor. Upper layer still good. Slightly attacked corium good and firm.	Same. Same, corium good.	About the same. Slight odor of ammonia and hydrogen sulphide.

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EXPERIMENT 40—CHANGES IN HIDES DURING DEPILATION IN STERILE SOLUTIONS.—(*Continued.*)

	Number I	Number II	Number III	Number IV	Number V
	Shaved	Hair on	Shaved	Hair on	Hair
Date	5 grams lime 0.15 gram AS_2S_3 400 cc. water	Same as Number I	5 grams of lime 400 cc. water	Same as Number III	20 grams 50 grams lime 800 cc. water
2–1	Upper layer gone in patches. Very mushy. Corium still firm. No odor.	Upper layer gone. No odor. Corium firm.	Upper layer mushy. No odor. Corium firm.	Upper layer almost all gone. Corium good. No odor.	Hair mushy. Same, hair mushy, some dissolved.
2–12	Upper layer all gone. Corium firm. No odor.	No odor. Corium firm. Slightly softer. Flesh side slightly swollen.	Upper layer partly gone. Corium better than I and II. No odor.	Upper layer practically gone. No odor. Corium good as Number III.	About the same, more hair dissolved.
2–25	Corium firm, no odor. Flesh side softer.	Corium firm, no odor. Flesh side softer.	Flesh side swollen a little. No odor. Corium good.	Flesh side swollen, no odor. Corium firm and good.	Stronger odor of ammonia, less odor of hydrogen sulphide.
3–2	Flesh side getting softer and swollen. Corium good not so firm. No odor.	Flesh side getting mushy. More swollen. Corium getting softer. No odor.	Flesh side getting mushy. Corium good and firm. No odor.	Flesh side quite mushy and swollen no odor. Corium good. Slightly softer.	About the same. Solution has a yellowish tinge.
3–9	Very glassy, mushy. Corium very much attacked. No odor.	Very glassy, mushy corium. Odor of hydrogen sulphide. Flesh side gone.	Peels in layers. More firm than Numbers I and II. Corium glassy. Mushier on flesh side. Very little odor.	Hair not dissolved, very slight odor of hydrogen sulphide. Corium still good. Glassy, flesh side mushy. Upper layer of corium can be scraped easily.	Weaker odor of ammonia and hydrogen sulphide. Considerable hair dissolved, some colloidal substance in suspension. Solution yellow.

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EXPERIMENT 40.—CHECK ON STERLITY OF SOLUTIONS AFTER TEN WEEKS.

Number of flask	I	II	III	IV	
Gelatine plates	—	—	—	—	Planted 2–12 examined
Gelatine tubes	—	—	—	—	Daily from 2–12 to 2–24
Beef tea tubes	—	—	—	—	
Pea-bean tubes	—	—	—	—	
Checks	+	+	+	+	
Anaerobic conditions. Litmus glucose gelatine in Novy jar over hydrogen	—	—	—	—	Planted 2-12 examined 2–26
Checks	+	+	+	+	

EXPERIMENT 40.—FINAL CHECK ON STERILITY OF SOLUTIONS.

Number of flask	I	II	III	IV	
Gelatine plates	—	—	—	—	Planted 3–9 examined
Gelatine tubes	—	—	—	—	Daily after 3–10 to 3–20
Beef tea tubes	—	—	—	—	
Pea-bean tubes	—	—	—	—	
Checks	+	+	+	+	
Anaerobic conditions on litmus glucose in a Novy jar over hydrogen	—	—	—	—	Planted 3–9 Examined 3–23
Checks	+	+	+	+	

EXPERIMENTS 41.

As a final check on the previous results the following tests were made: Two flasks were plugged with cotton, sterilized by dry heat for 1 minute at 200° C. To each flask 100 cc. of water and 10 grams of lime were added. They were then autoclaved 20 minutes at 110° C. Two pieces of calfskin 1 x 2 inches were sterilized 48 hours in a Seymour-Jones solution. The sterile hides were placed in the flask October 30, 1913. The flasks were left undisturbed at room temperature until March 9, 1914, when they were opened and sub-cultures made as in previous experiments. All sub-cultures were negative but the checks were positive. The flask, therefore, contained a sterile solution.

The skin had changed considerably in its 4 months treatment in sterile lime. The hair was all very loose; the upper layer and the flesh side of the skin had become mushy and swollen. The corium was fairly firm but glassy in appearance. No odor was noticeable. The preceding experiments had all been made on calfskin. In order to check the results on heavier hides a sample of sterilized cowhide was placed in a sterile lime solution Decem-

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ber 12, 1913. This contained 5 grams of lime and 0.5 gram of sodium sulphide in 100 cc. of water. The hide was examined March 9, 1914. The flask had been left undisturbed during this time. Sub-cultures were made as before, and all results were negative. This showed that the solution was sterile.

This hide had also changed materially by its 3 months' treatment in sterile lime. All the hair was dissolved. The upper layer had been dissolved and the flesh side had not only become mushy as in the previous experiment, but in fact it had disappeared, leaving only a firm tough layer of corium, which had apparently suffered very little change.

Depilation in Sterile Solution and Subsequent Tannage.

After these preliminary tests of liming under sterile conditions, somewhat larger pieces of hide were used and carried through the entire tanning process. The final products were then compared with commercial products obtained by liming in the usual manner.

The first experiments were on pieces of cowhide which were tanned subsequently, through the courtesy of Mr. V. A. Wallin, in the Wallin tanneries at Grand Rapids.

Experiment 42. Experiments on Cowhides.

Two pieces of cowhide about 1 x 10 feet were sterilized 3 days in Seymour-Jones's solution. The bottles in which the previous solutions had been sterilized had been made of cheap cast glass but had caused much trouble by breaking during sterilization, in spite of the utmost precautions taken while heating and cooling them. This difficulty was overcome by using narrow and deep galvanized iron cans 5 centimeters by 42 centimeters by 46 centimeters. Small shelves were arranged so the hides could be suspended over glass rods. The solutions to be used were sterilized in these cans by boiling over a direct flame for 4 to 8 hours. The cover, not fitting tightly, allowed a cloth moistened with 0.02 per cent. mercuric chloride solution to be placed over the can in such a manner that it could be kept sterile.

Hide No. 1, was limed in a solution containing 5 grams of lime and 0.5 gram of sodium sulphide crystals, in 400 cc. of

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water, for 3 days. It was removed while slightly underlimed and placed in a can containing a sterile saturated lime solution and shipped to the Wallin Tannery, Grand Rapids, Michigan, to be put through their regular tanning process.

Hide No. 2, was limed in the same kind of a solution as No. 1 but for 6 days. It was removed and shipped in a sterile saturated lime solution. Sub-cultures made as in previous experiments gave negative results and showed that these hides had been unhaired in sterile solution.

The finished sample of leather from hide No. 1 was returned from the tannery with the comment:

"The job seems to be satisfactory. The stock is a little bit snappy on the grain but it is not certain that this has any relation to the liming."

The finished sample of leather from hide No. 2 has not yet been returned from the tannery.

Experiment S-43.

Two pieces of cowhide were received wet and salted. They were washed thoroughly in water and sterilized in Seymour-Jones solution for 48 hours. The limes used were made up by dissolving 5 grams of lime and 0.5 gram of sodium sulphide in 400 cc. of water. They were sterilized by boiling 4 to 8 hours over a free flame. The hides were now treated as follows: One piece was limed 4 days, then placed in a sterile saturated lime solution and shipped to the tannery. The other piece was purposely overlimed and after 7 days in the lime was sent to the tannery in the same way as was the other piece. Sub-cultures from the limes used, were made on various media in the same manner as in previous experiments. All sub-cultures were negative and showed that the solutions had been sterile.

The loss of hide substance in the liming process is often considerable and an examination was made of some of these lime solutions to determine the amount of hide substance dissolved. For comparison an old lime from the Wallin tannery was also tested. The hide substance in solution was calculated from the content of ammonia shown by the Kjeldahl method. The results are shown in the following table:

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HIDE SUBSTANCE DISSOLVED IN LIMES.

Source of lime	Ammonia g. per l.	Hide substance g. per l.	Remarks
Experiment 42	0.1366	0.623	Hide 3 days in
Hide #1.	0.1326		sterile lime.
Experiment 42	0.3145	1.457	Hide 6 days in
Hide #2.	0.3155		sterile lime.
Experiment 43	0.4114	1.909	Hide 4 days in
Hide #1.	0.4138		sterile lime.
Experiment 43	0.9479	4.376	Hide 7 days in
Hide #2.	0.9452		sterile lime.
Old lime from Wallin tan	1.439	6.694	
	1.454		

The amount of hide substance dissolved by these sterile limes is less than that shown in the old lime from the tannery but not enough is known of the changes of limes with continued use to warrant a positive conclusion.

EXPERIMENTS ON CALFSKINS.

Calfskins received in the dry salted state were unhaired in sterile limes and through the courtesy of Mr. Carl E. Schmidt, tanned by the chrome process in his Detroit tannery.

Considerable difficulty had been experienced in handling the can used to contain the sterile limes in the previous experiments, and spots appeared on the hides where they touched the metal. The calfskins were limp enough so that glass vessels could be used.

EXPERIMENT S-41A.

A bottle of about 6 liters capacity was plugged with cotton and sterilized at 200° C. for 1 minute in a dry heat sterilized. One-half of a small calfskin, weighing 250 grams was sterilized 24 hours in a Seymour-Jones solution. A lime solution containing 5 grams of lime and 0.15 gram of red arsenic sulphide in 400 cc. of water was put into the sterile bottle and this was autoclaved at 110° C. for 20 minutes. The sterile skin was now placed in the sterile lime and left for 9 days. The hair slipped very easily. This skin was sent to the Carl E. Schmidt Tannery at Detroit, Michigan, where it was chrome tanned and finished. The product was of little value. The grain could be peeled off easily. The leather had very little strength and felt very thin. The liming had been allowed to proceed too long and the skin had become seriously damaged. The grain was also drawn and harsh.

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In subsequent tests on calfskin a large Jena flask of about 15 liters capacity was plugged with sterile cotton. The flask was too large to permit sterilization in a dry heat sterilizer hence it was only washed with distilled water. The cotton plug, after it was made to fit the flask was sterilized for 5 minutes at 200° C. A lime solution was made containing 5 grams of lime and 0.15 gram of red arsenic sulphide per 400 cc. of water, and put into the flask. This was then autoclaved 4 to 5 hours at 110° to 120° C.

EXPERIMENT 44.

One-half of a small calfskin was sterilized 48 hours in Seymour-Jones's solution. It was then placed in the sterile lime solution in the sterile flask and allowed to remain 5 days. The hair was partially destroyed and slipped easily, except in certain spots. These spots were very difficult to unhair for some reason. The grain of this leather cracked and scuffed easily and was not satisfactory.

EXPERIMENT 45.

The flask used in Experiment 44 containing the same lime and arsenic sulphide solution, was autoclaved 4 to 5 hours at 110° to 120° C., to insure sterility of the contents. One-half of a dry salted calfskin which had been sterilized for 24 hours in a Seymour-Jones solution, was added to the cooled flask with sterile forceps. This skin was limed 6 days. Sub-cultures made precisely as in previous experiments showed negative results and that the limes had been sterile. The skin unhaired easily except in one place an area of about 6 square inches. The white hair on this spot adhered with remarkable tenacity while the black hair on the rest of the skin slipped easily. No explanation of this peculiar occurrence could be suggested at the tannery. The hide felt "full" and the final product was of fair quality. The leather had average tensile strength and a good grain although it did not feel as full as the standard product of the tannery. Stretching did not crack the grain of the final product except on the extreme flank.

EXPERIMENT 46.

To the same lime solution in the flask of Experiment 45 9 grams of red arsenic sulphide, 300 grams of slaked lime and

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enough water were added to bring the contents up to the original volume. This flask was again autoclaved 4 to 5 hours at 110° to 120° C. to insure sterility of the contents. The piece of calfskin to be used was sterilized as before in a Seymour-Jones solution for 24 hours. The hair slipped easily after 6 days. Sub-cultures made from this lime solution, on various media as in previous experiments, showed negative results and proved the solution to have been sterile. The final leather felt quite "full" in the judgment of the tannery superintendent. It had a good grain and a tensile strength greater than that of the average skin limed in the ordinary manner. It had a very slight harshness which could probably be overcome by modification of the finishing process. The leather felt very full both in the flank and at the backbone. The flank appeared to be better than in the ordinary product.

Conclusions.

The foregoing paper studies from three different viewpoints the changes taking place in hides during their conversion into leather and particularly during the liming process. A study is made of structural changes throughout the vegetable and mineral tanning processes as shown by the microscope; of gross changes in volume, weight and density of the skin; and of the practicability of carrying out the depilation process in sterile solutions.

Detailed methods have been worked out for the satisfactory preparation of microscopic sections both by the colloidin and freezing methods. A study of numerous sections of skin shows that the structural changes occurring during depilation and tannage are so gradual that only the broad outline can be followed. The inter-fibrillar substance in the bundles of connective tissue dissolves in the liming process and the fiber bundles split up into their component fibrils. The flank is composed of larger, fewer and more irregular fiber bundles with larger interstitial spaces than the better portions of the skin. This gives a partial explanation of the poorer quality of flank leather.

When dry calfskins are put into water they increase in superficial area, thickness and weight but decrease in density. The area remains almost constant during the liming process in bacterial limes, but the volume and hence the thickness of the skin increases quite consistently and at a decreasing rate during the

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liming process. The weight increases at approximately the same rate but a study of the relationship of weight and volume as shown by the density curves, indicates that the volume increases faster than the weight during the first 4 or 5 days in limes containing bacteria so that at the end of this period the hide shows the minimum density which it ever attains in the limes. Within 2 days after this point is reached the volume decreases more rapidly than the weight and the density rises decidedly. The significance of these points of inflection of the curves is not evident.

Both volume and weight decrease in the feebly acid bate used but the decrease in weight is greater than that of the volume so that the density falls. In the pickle, conditions are the reverse of those in the bate and the density rises sharply. No great changes in weight volume or density occur during the one bath tannage used.

Different pieces of the same skin while the same in general, show decided quantitative variations from each other. The shoulder, back and rump show distinct differences which are not constant in different skins. The flank, however, swells quite consistently more than the rest of the skin, both in water and in the limes. These differences may be due to the varying thickness of the skin or to surface conditions such as fat. If the flesh side is painted with a soap solution before immersion in the limes so that an insoluble lime soap is precipitated upon it, the swelling is greatly increased.

It has been shown that it is possible to depilate a skin or hide under strictly sterile conditions with lime alone or with the addition of sulphides. The same sterile lime solution can be used to depilate successive pieces of hide. Calfskin kept for 6 months in sterile milk of lime shows a firm though rather glassy corium. A skin kept a similar length of time in sterile milk of lime containing arsenic or sodium sulphide, is completely dissolved. The hair from the skins in the latter solutions is also dissolved completely, while that of the skin in lime alone, appears almost unchanged.

Pieces of cowhide and calfskin unhaired under sterile conditions have been tanned and finished in commercial tanneries using vegetable and mineral tanning agents, with fair results. It seems entirely probably that with a little more experience in handling

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sterile limes a good product, equal in all respects to that produced by the present methods of liming could be obtained.

BIBLIOGRAPHY.

1. Jettmar, Handbuch der Chromgerbung (1900).
2. Der Gerber.
3. Procter, The Principles of Leather Manufacture.
4. Procter, The Leather Industries Laboratory Book.
5. Collegium.
6. Bulletin de la Societe d'encouragement pour l'industrie. Nationale.
7. Dinglers Polytechnische Journal.
8. Hyde, Diseases of the Skin (1909).
9. JOURNAL of the American Leather Chemists Association.
10. Warthin, Practical Pathology.
11. Journal of the Society of Chemical Industry.
12. English Patent Number 2873.
13. Villon, Traite de la Fabrication des cuirs.
14. Leather Trades' Review.
15. Bull. Syndicat. Gen. Cuirs et Peaux, p. 416, Nov. 10, 1908.

(EDITORS' NOTE. Mr. Schlichte's conclusions in regard to the possibility of unhairing in sterile limes containing no other chemicals are so radically different from those of other observers, as mentioned in Mr. Bennett's paper in the November issue, that the Editors thought he might be in error as to the actual sterility of his lime liquors after the pieces of hide had been in for a considerable time and several tests had been made on the condition of the hide by opening the vessels. We considered it possible that while the vessels were open, bacteria from the air might have entered, grown in the liquors and caused unhairing, but refused to grow in any of the four media which Mr. Schlichte used in his tests. Mr. Schlichte replies that the precautions taken were the same which he has used in very many experiments, and the proportion of contaminated cultures has been only one in 2,500, so that the probability of our suggested explanation having any basis in fact is extremely slender. He also meets our suggestion that each sample ought to be left unopened until the expiration of the whole period, separate samples being set for each period, by pointing out that in his experiment 41 two flasks were charged and left unopened for 5 months. We hope that the partisans of the bacterial theory will bestir themselves, and that further experiments will be carried out which shall settle the question one way or the other to the satisfaction of all concerned.)

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RESEARCH LABORATORY.

The Committee of the National Association of Tanners on the subject of the establishment of a research laboratory submitted a report to the annual meeting of the Association held in Chicago, Oct. 29, 1915. The report was adopted, and a Finance Committee appointed to see if the necessary funds could be raised. The report of the Committee is entitled "Report on Suggested Plan and Organization of Proposed Investigation and Research Division of Tanners Institute," and is as follows:

PLAN.

These suggestions contemplate the organization and conduct of a bureau of investigation and research which shall deal scientifically with technical and practical problems incident to the manufacture of leather for industrial purposes in the United States. It is proposed that this work be organized as an Investigation and Research Division of Tanners Institute and that it be conducted at Pratt Institute in conjunction with the educational work of Tanners Institute, constituting an enlargement in scope and extension of the investigation work heretofore conducted at Pratt Institute under the auspices of Tanners Institute. In the event of the adoption of this or a similar proposal Tanners Institute will then consist of two divisions:

(*a*) Education Division, comprising the courses of instruction organized and conducted at Pratt Institute for nearly four years past:

(*b*) Investigation and Research Division, as hereinafter outlined.

It is also contemplated in these suggestions that the investigations and researches to be undertaken should be limited to matters of general interest and value to the industry, which have been duly presented to a committee suitably representing the industry, and by this committee approved for carrying out at the expense of Tanners Institute. This conception of the kind of work to be undertaken by the Investigation and Research Division excludes the handling of special problems for private interests. In short, the subjects for investigation and research would be selected with reference to the welfare of the industry as a whole, and the expense would be borne by the general funds of

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Tanners Institute. While thus eliminating technical expert and consulting work for private interests, the limitation here proposed would not interfere with the taking up of problems of interest to different divisions of the industry; as for illustration, matters of particular interest to heavy leather manufacturers in one case, or subjects relating to light leather manufacture in another case, and other general divisions of the industry likewise. It is the presumption that all subjects approved for investigation and research would be of direct value to the largest possible number of leather manufacturers and that the results would be applicable in a practical way and published in such manner as to be available to the entire industry.

Control.

It is suggested that the control of the proposed Investigation and Research Division of Tanners Institute be vested in an Advisory Committee appointed by and suitably representing the National Association of Tanners and the American Leather Chemists Association, the actions of this Committee to be subject to the approval and direction of each association to whatever extent may be deemed advisable. This Committee subject to prescribed procedure shall receive and act upon the recommendations and reports of a chief chemist who shall be in direct charge of the work of investigation and research as hereinafter described. The Committee shall appoint the chief chemist and shall receive and act upon his annual recommendations concerning appropriations and expenditures.

Technical Direction.

The technical direction of the Investigation and Research Division shall be placed upon a chief chemist who shall recommend to the Advisory Committee subjects for investigation and research and shall report upon work done. He shall present to the Committee annually a report upon each year's work and personnel of the Investigation and Research Division, and shall also annually present an estimate of appropriations required for the ensuing year.

All formal recommendations and reports of the chief chemist shall be countersigned by the expert consultant who shall also act in an advisory capacity to the chief chemist as requested.

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RECOMMENDED BUDGET OF PROPOSED INVESTIGATION AND RESEARCH DIVISION OF TANNERS INSTITUTE.

Technical Direction and Contingent Expense:	
Chief Chemist Expert Consultant Contingent expense	$7,025.00
Additional Staff:	
Bacteriologist (about)	1,500.00
Graduate technical assistants, 2 @ $600.....	1,200.00
Supplies and Materials:	
Hides, skins and tanning materials (less receipts for leather sold)	300.00
Chemicals and renewals	500.00
Electricity and gas	200.00
Rent of floor space for laboratories, including heat, water and janitor service, 1,500 sq. ft. at 35 cents per sq. ft.....	525.00
Equipment—initial equipment $2,500, distributed over five years (While this entire amount, $2,500, would have to be expended at the start, it is for convenience of estimate here set down as if distributed equally over the first five years.)	500.00
Traveling expenses	250.00
Total of Investigation and Research Division.....	$12,000.00

Chief Chemist.—The chief chemist should be a man who has had extensive experience in research work relating to leather manufacture. He shall devote his entire time to such investigations as may be approved by the Advisory Committee. In the actual conduct of the work of investigation and research he should be allowed sufficient latitude to enable him to secure best results.

The work of the chief chemist and of his staff should continue throughout the entire twelve months, with proper allowance for vacations. It is believed that a suitable man for this position could be secured at a salary somewhat between $4,000 and $7,500, though these figures should not be regarded as defining the salary limits of this position. The success of the investigation and research work would depend almost entirely upon the capability and devotion of the chief chemist, and it would therefore seem advisable not to specify in advance any definite salary limits for fear of prejudicing the securing of the proper man for the position.

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Expert Consultant.—The functions of the expert consultant have been described above, and it is contemplated that this position shall be occupied by Dr. Allen Rogers, in addition to the performance of the regular duties of his position as an instructor in Pratt Institute.

An annual fee for these services is proposed, and $500 has been mentioned, though not definitely proposed, as perhaps a proper amount.

Contingent Expenses.—Owing to the impossibility of including and accurately estimating in advance all expense necessary to the accomplishment of the ends for which the investigation and research division is proposed, it is recommended that $6,500 to $8,500 be set aside to cover the salary of chief chemist, expert consultant and contingent expenses, these items being lumped together for convenience of estimation and to avoid too narrowly defining the chief chemist's salary, for reasons above explained.

Additional Staff.

In addition to the chief chemist and expert consultant, it is suggested that the staff shall consist of a bacteriologist, two graduate technical assistants, and a stenographer.

Bacteriologist.—A competent bacteriologist is contemplated. It is essential that he should have experience in leather work. It is believed that a satisfactory bacteriologist can be secured at a salary of from $1,500 to $1,800 per year.

Graduate Technical Assistants.—These men should be appointed from graduates of the Applied Leather Chemistry course and their employment would be somewhat in the nature of a post-graduate course or apprenticeship. They would be under the orders of the chief chemist, who would assign to them definite work in accordance with his judgment. They should start on the first of July and serve for one year. Should additional men desire to go into the laboratory, they might be allowed to do so, if feasible, but without pay. It should be a condition that these men must have been students for at least one year at Pratt Institute and be graduates of the Applied Chemistry or the Applied Leather Chemistry course. It is suggested that the paid assistants be two in number and receive $600 per year.

Supplies and Materials.—It is roughly estimated that hides,

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skins and tanning materials would be required to an amount costing from $300 to $500 per year, net expenditure after deducting amount of saleable hides; chemicals and apparatus about $400 per year; and electricity and gas, $200 to $300 per year. These expenses will, of course, depend upon the actual amounts used.

Laboratories.—For the accommodation of the proposed laboratories which would be used exclusively for investigation and research work by the chief chemist and his staff, it is estimated that about 1,500 square feet of floor space would be required. Two locations have been suggested: (*a*) The chemistry building of Pratt Institute; and (*b*) A neighboring high grade factory building, of which several are available in the immediate vicinity.

The Trustees of Pratt Institute have not passed upon the suggestion to rent space in their chemistry building, and it has not been positively ascertained that they could spare space for this purpose, although it seems probable that this might be arranged. The chemistry building is in many respects the more convenient of the two locations suggested and would seem decidedly preferable as advantageously combining convenience and close association with the Educational Division of Tanners Institute.

As an alternative location for the research laboratories in the event of the chemistry building not being available, it has been ascertained that suitable accommodations could be arranged in a neighboring factory building at a rental of about 35 cents per square foot, or $525 per year for 1,500 square feet, including heat, water and janitor service. If space in the chemistry building should be available, the rental would probably be fixed at the same figure, which would be a nominal rate, as the real rental value of the chemistry building would be considerably higher.

Pratt Institute's school tannery would in any event be available without charge for experiments in the tanning and finishing of leather under the direction of the Investigation and Research Division; and Pratt Institute instructors and tanning course students would co-operate in the actual carrying out of experimental tanning operations without charge. Four years ago Pratt Institute expended about $4,000 for the extension of its school tannery, and now contemplates a further outlay of about $7,500 for the proposed transfer of the school tannery to the basement of the

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chemistry building and its reinstallation on an enlarged and improved plan including considerable new equipment.

Equipment.—Laboratory fixtures, such as chemical tables. sinks, hoods and plumbing, would have to be provided. It is estimated that adequate fixtures of good quality, though not the most expensive grade, could be obtained and installed for about $1,600. In addition to the fixtures a considerable amount of chemicals and research laboratory equipment would be needed, and it is estimated that about $900 would be required for this purpose. The above two equipment items total $2,500, and while this entire outlay would have to be made preliminary to starting the regular work of the laboratory, the total amount, $2,500, has been set down in this estimate as if distributed over five years, or $500 per year on this basis. It would be necessary also to make provision for annual renewals and for some extension of equipment, for which, perhaps, $300 additional per year would be needed, making the total amount of equipment $800 per year for each of the first five years.

Traveling Expense.—It is suggested that an appropriation of $250 be made to cover traveling expenses of the chief chemist or members of his staff in connection with attending conventions for the purpose of making personal reports, presenting papers, etc.

Appended to the report is a letter from F. W. Kressman of the Forest Products Laboratory, Madison, Wisconsin, to A. H. Lockwood of the *Shoe and Leather Reporter*, extracts from which follow:

"In further reference to your letter of June 4th regarding the establishment of an endowed research laboratory by The National Association of Tanners in conjunction with the American Leather Association:

"On looking up this subject at some length I have been able to find only three organizations which are somewhat analogous to the institution which you have planned. These are the Scientific Section of the Paint Manufacturers Association of the United States, the Underwriters Laboratories, Inc., under the direction of the National Board of Fire Underwriters, and the research laboratory of the National Canners Association, 1739 H. Street,

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N. W., Washington, D. C., of which Dr. W. D. Bigelow is the director. I wish to refer you to Mr. G. B. Heckel, Secretary of the first association, 636 The Bourse, Philadelphia, Pa., who, no doubt, will be able to give you more complete information regarding this association, which is made up of a great many of the paint manufacturers of the United States, and the work of the Scientific Section which is under the direction of Dr. Gardner, who I believe is also at present connected with the Institute for Industrial Research at Washington, D. C. The principal offices and testing stations of the Underwriters Laboratories are located at 207 East Ohio Street, Chicago. The building and its equipment are valued at approximately $175,000, and several years ago employed 83 people, most of whom were technical men. The laboratories issued a small booklet giving general information regarding its organization, its purpose, and its methods, which can be obtained by writing to Mr. W. H. Merrill at the Chicago offices. This laboratory, which has branches in many cities, is a corporation which is not in business for profit, since it receives its chief financial support from the National Board of Fire Underwriters under whose general direction the work is carried on. The work is confined to investigations having a bearing upon the fire hazard and is undertaken as one means of securing correct solutions of many of the problems presented by the enormous destruction by fire of property in this country. The laboratory of the Canners Association has issued a number of bulletins of interest to the canners, such as the causes of "swells" and "springers," which are the terms applied to swelled and sprung cans. They have also investigated the manufacture of tomato pulps and catsups so as to give the public a more uniform and standard product.

"In addition to these institutions, there is a long list of other laboratories which are not co-operative in the sense that they belong to the industry as a whole, but are research laboratories which have been built up by particular industries to solve the problems arising in their respective fields. Probably foremost in this direction is the research laboratory of the General Electric Company, of Schenectady, N. Y., of which Dr. W. R. Whitney is the Director. At present, I understand that as high as $800,000 a year is being used for laboratory work, a considerable

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part of which is devoted to research. A large number of the most recent electrical improvements, among them the Mazda tungsten lamps, are the direct result of work which has been accomplished here, and I wish to refer you to an article by Dr. Whitney on the organization of industrial research in Volume 32, page 71, of the *Journal of the American Chemical Society*.

"In Volume 10, pages 140-146, of *Metallurgical and Chemical Engineering* you will find a symposium on research in which Dr. A. M. Comey, Chief Chemist of the Eastern Laboratory at Chester, Pa., of the E. I. du Pont de Nemours Powder Company, presents a paper on certain phases of technical chemical research.

"The Eastman Kodak Company has a large research laboratory of which Dr. Mees is the director.

"Another large research laboratory is that of the Standard Oil Company at Whiting, Ind., where probably $250,000 is spent annually on research. In addition, all of the large steel companies have chemical laboratories, both for analytical and control purposes, and also research laboratories. Perhaps the finest of these is that of the American Ingot Iron Company at Middletown, Ohio.

"The Mellon Institute at Pittsburgh, is an example of university research which is combined directly with the industry by the founding of scholarships by different industrial concerns. These scholarships vary from several hundred dollars to $20,000 or more annually, depending upon the nature and size of the problem, and at present some two dozen scholarships are in operation.

"Among the other large research laboratories that may be mentioned are those of the large electrochemical companies at Niagara Falls. The laboratories in connection with the meat-packing establishments in Chicago, whose researches have developed the production of a very large number of products and the complete utilization of the carcass of the slaughtered animal.

"I am enclosing a pamphlet describing our own organization here, which is a laboratory devoted entirely to research on the uses and properties of wood other than for lumber purposes. Since the National Government is one of the largest timber holders in the country and is directly and commercially interested in the sale of this material and its proper commercial use, it has

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found that an organization of this kind is necessary, not only for its own purpose but also for the instruction of the public in general regarding the proper uses for wood and the proper woods for particular uses."

TANNERS INSTITUTE FOURTH ANNUAL REPORT.

The fourth annual report of the Institute has been published by the National Association of Tanners, and may be had from the Executive Secretary, Mr. Cudworth Beye, 212 West Washington Street, Chicago. It is an attractively gotten up pamphlet of 22 pages, embracing the following topics: Organization and aims of the Institute, list of students graduating in 1915, with present location, award of scholarships, prizes, brief statement of observation trips given during the year, proposed exhibit at the Shoe and Leather Fair in Boston, list of lectures given during the year, list of investigations carried out or in progress, financial statement, description of new tannery, with illustration and plan, statement of the work of the Advisory Committee, acknowledgment of gifts, enumeration of the entering classes, and prospectus of the courses offered.

The class graduating in the tanning course numbered 17, ranging in age from 17 to 28 years. Nine had had previous experience in leather manufacture, and only three were without practical experience of some kind. All but two were placed at the time the report was prepared. There were four graduates in the course in applied leather chemistry, ranging in age from 22 to 27 years. One of these was a graduate of Pratt Institute, one of Haverford College, one of Pennsylvania State College and one of the University of Wisconsin. One of these is now an instructor at Pratt, one is a graduate student in chemistry at Columbia, and the other two in commercial positions.

It is proposed to send to the Shoe and Leather Fair in Boston in 1916 an exhibit consisting of a model tannery laboratory in operation.

Since the foundation of the Tanners Institute, the school tannery has been located on the top floor of the chemistry building of Pratt Institute. More space being needed, the entire basement of the same building has now been set apart for this pur-

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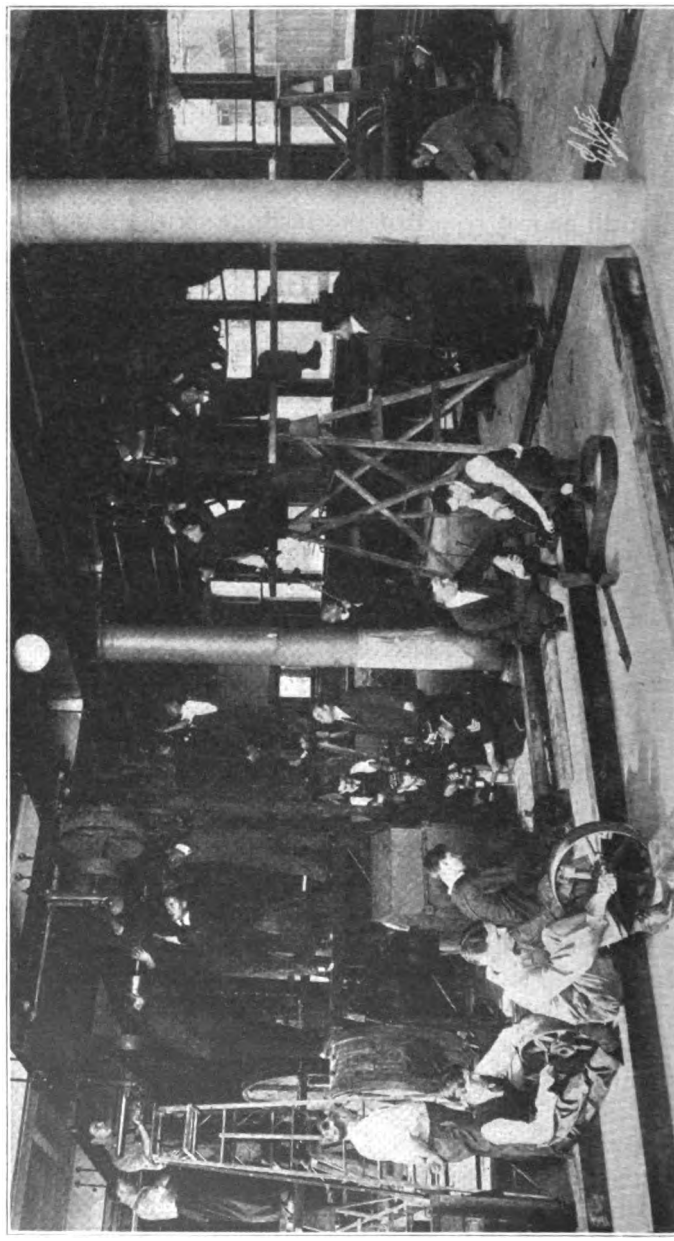

STUDENTS AT WORK INSTALLING EQUIPMENT IN NEW TANNERY.

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pose, with some additional space in an adjoining building. The main tannery is about 122 feet long and 42 feet wide. The accompanying cut shows students at work installing equipment. The entrance hall is fitted with cabinets for exhibits of leather and tanning materials. There are lockers and a dressing room, lavatory, tanning materials stock room, finished leather stock and measuring room, drying and tacking room, buffing room, and a large room, embracing more than half of the whole floor space, equipped as a beamhouse, chrome department, tan yard and finishing department. Besides the increased space, considerable additions are being made to the machine equipment. It is believed that when the new installation is completed, the tannery will compare favorably with the best school tanneries abroad.

The Advisory Committee, made up of members appointed by the National Association of Tanners and members appointed by the American Leather Chemists Association, has been of assistance to the Institute in various ways during the year. The Committee has met at the Institute three times during the school year and in consultation with representatives of Pratt Institute has considered the various matters bearing upon the welfare of the school. This Committee formulated a plan for the establishment of a research department, which has been adopted by the National Association of Tanners, and is presented elsewhere in this issue of the JOURNAL.

THE ORIENTAL MANUFACTURE OF GAMBIER.* PART II.

By Alexander T. Hough.

In the first part of this article (see this J., pp. 573-9), I described in detail the manufacture of cube gambier, as carried out by the Chinese in the Malay States, and will now proceed to illuminate the subject with the light of science, which throws into relief many interesting details that might otherwise escape observation.

At all points in the process, where possible, samples of the materials and products were taken with a view to analysis and microscopic examination. These investigations have now been completed, except in the case of the Borneo rice meal, *dada,*

* *Leather Trades' Review*, Oct. 13, 1915.

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which was evidently very moist, and was completely permeated with mould on arrival in England. However, other samples of Burmese and Siamese meal have been obtained, which do not seem to differ appreciably from the Bornean in microscopic features.

The analyses are as follows:

	True gambier leaf. Per cent.	Spent gambier leaf. Per cent.	Wild gambier leaf. Per cent
Tannin	5.5	2.6	5.7
Non-tannins	3.3	2.5	3.8
Insoluble	29.2	32.9	28.5
Water	62.0	62.0	62.0
	100.0	100.0	100.0
Red	6.2	—	15.4
Yellow	28.8	—	55.8

	Liquor before adding rice. Per cent.	Liquor straining through mould Per cent.	Final product "cube" gambier Per cent.
Tannin	13.7	7.5	35.0
Non-tannin	11.0	7.2	31.0
Insoluble	0.6	0.3	21.9
Water	74.6	85.0	12.1
	100.0	100.0	100.0
Red	1.6	—	2.0
Yellow	4.7	—	5.4
Specific gravity	—	1.063	—

In reference to these analyses, it might be mentioned that the leaves were, of course, brought to Europe after having been previously dried. The moisture of the gambier leaf was estimated in Borneo, and showed 62 per cent., as indicated. Other leaves of various trees and shrubs previously examined by the author having usually shown between 60 per cent. and 65 per cent. of moisture, it was thought wise to adopt this figure, in the absence of actual analysis, for the wild gambier, and also to calculate the spent leaf on this basis, so that all the analyses should be strictly comparable.

The two liquors were preserved by adding a few drops of chloroform, which kept them in perfectly good condition. The moisture in the two liquors as estimated in Borneo was respectively 74.3 per cent. and 83.5 per cent., and the specific gravity

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of the strained liquor was 1.077. There was no trace of mould or fermentation on opening.

From the above figures we see that more than 50 per cent. of the total available tannin in the gambier leaf is lost through two channels; first, through the spent tan, and, secondly, through the liquor percolating through the mould, of which there is a considerable quantity.

Apart from this latter loss 2.9 per cent. of the total tannin is extracted, so that in order to produce 1 ton of cube gambier the Chinese manufacturer is obliged to boil 12.07 tons of cuttings. Therefore, to yield any considerable output, an enormous plantation is required. Most of the Chinese plantations have only one pan working, and do not produce 1 cwt. per day. The largest plantation of which I inquired was working three copper boilers and producing 5 tons per month. The proprietor was a dollar millionaire, whose ideas were sufficiently advanced to replace the old iron pans with copper ones, but he had no wish to further improve his product or to export it, for reasons previously given.

In fact, it is worth remarking that the Chinese product, crude as are the methods of manufacture, does not leave much room for improvement in so far as quality is concerned, when compared with the European manufacturers' plantation gambier, such as is produced in Sumatra.

If we calculate the Chinaman's "liquor before adding rice" on to the same moisture basis as average plantation gambier, we see that the two products are practically identical. The insoluble in the Chinese liquor shows up very favorably, but would probably increase a little upon concentration.

	Chinese liquor calculated to moisture indicated		Plantation gambier No. 1.	Plantation gambier No. 2.
	Per cent.	Per cent.	Per cent.	Per cent.
Tannin	37.2	38.8	36.4	40.6
Non-tannin	29.9	31.2	29.5	28.5
Insoluble	1.9	2.0	3.1	2.9
Moisture	31.0	28.0	31.0	28.0
	100.0	100.0	100.0	100.0

As regards other constituents of gambier, I would call attention to a paper by Puran Singh, *J. S. C. I.*, March 15, 1915 (this J., p. 421), "Note on the Addition of Fat to Tannin Extracts,"

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in which he points out that tanning materials making harsh leather contain less natural fat than those yielding a soft leather, whilst at the same time his figures prove that very little of this fat is extracted in leaching.

There seems to be very little in the contention that the natural fat in the bark influences the mellowness of the leather, which is rather due to the nature of the tannin, except perhaps in the case of gambier, where the fat is in suspension. The figures show that gambier contains by far the greatest percentage of fat, from 0.8 per cent. to 1.6 per cent. and the reason for this is not far to seek. It is not natural to the plant, but is introduced in the rice dust, which contains considerable quantities of fat.

Another important constituent of gambier is nitrogen in the form of protein or albuminoids. Although a certain proportion is naturally present in the plant, a far greater quantity is introduced in the rice dust. The analyses of rice meal are as follows:

	Burma meal Per cent.	Borneo meal Per cent.
Moisture	9.9	12.7
Nitrogen	2.07	2.43
Albuminoids (N × 6.25)	12.96	15.194

The nitrogen was also estimated in the "liquor before adding rice," and the cube gambier made from it. To strictly compare the nitrogen in both, the quantity contained in the liquor was calculated on a basis of 35 per cent. tannin, the strength of the cube gambier, with the following results:

	Liquor 13.7 per cent. tan. Per cent.	Liquor 35 per cent. tan Per cent.	Cube gambier Per cent.
Nitrogen	0.1575	0.402	0.9307
Albuminoids	0.9844	2.51	5.82

If we now subtract the albuminoids in the liquor from the albuminoids in the cube, we get the albuminoids introduced in the rice, namely, 5.82 — 2.51 = 3.31 per cent. If we conclude, as we may very safely do, that nearly the whole of the insoluble matter in the cube gambier, which was manufactured with the Borneo meal, is due to this, it will be seen that the figures are confirmed in a most remarkable manner.

The meal contains 15.2 per cent. albuminoids, and the gambier contains 3.31 per cent. due to meal; therefore the percentage of meal present in the gambier should be: 3.31 × 100 ÷ 15.2 =

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21.7 per cent. whilst the quantity of insoluble in the cube gambier is 21.9 per cent. by actual analysis.

It might be suggested that gambier probably owes some of its mellowing properties to the rice meal, as the amyloids certainly are a cause of fermentation, and farinaceous matters, introducing both albuminoids and starch, are in current use in the production of the softer leathers.

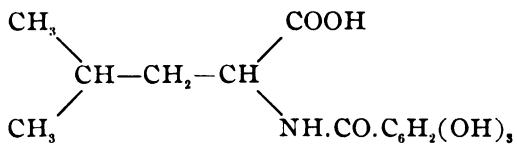
There are several plants called "wild gambier" by natives in different parts, and these are usually boiled down for chewing purposes. The sample analyzed was brought to me by Dyaks, and is known locally as *Kyte-kyte*, but other plants are also known by this name. It was identified in Singapore Botanical Gardens as an *Uncaria*, but further specific identification was impossible. It is equal to gambier in tannin strength but much inferior in color, and the tannin is wholly catechol.

THE FORMATION OF ELLAGIC ACID FROM GALLOYL-GLYCINE BY PENICILLIUM.*

By M. Nierenstein.

From the Biochemical Laboratory, Chemical Department, University of Bristol.

Kraemer (1900), who investigated the galls formed by *Cynips aciculata* on *Quercus cocinea*, found that during the chrysalis stage gallic acid was produced and that as the imago developed the gallic acid gave place to tannic acid. These observations gain in interest if viewed in the light of the recent investigations of v Stockert and Zellner (1914), who have proved the presence of nitrogenous products in a number of galls caused both by insects and fungi,† and also of the results of Nierenstein (1914) who has isolated galloyl-leucine



* *Biochemical Journal*, (Vol. IX, No. 2, June, 1915), *Collegium*, (London), 1915, pp. 276-9.

† With reference to gall formation see E. T. Connold, (1908-1909.)

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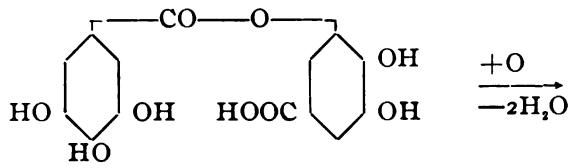
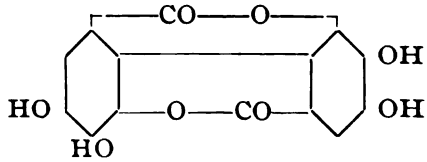
from the galls of *Quercus aegilops,* which are caused by *Cynips calcis.* These investigations suggest, namely, the possible formation of the digallic acid nuclei in tannic acid by way of some nitrogenous product of the galloyl-leucine type which serves as foodstuff for the growing parasites and at the same time leads to the formation of digallic acid, the presence of which in the tannic acid molecule has been established by Nierenstein (1910, 1 and 1912, 1) and which has been synthesised by Emil Fischer and K. Freudenberg (1913), so that the identification of this substance, if experimentally formed, was possible. The conditions selected as a preliminary to other investigations in progress were inquiries into the action of *Penicillium* on galloyl-glycine, which is easily prepared by the usual methods of Emil Fischer. There was, of course, the possibility, especially in the light of the beautiful investigations of Lewis Knudson (1913) on the action of fungi on tannic acid, that the digallic acid, if formed, would at once be decomposed into gallic acid; however, the selected conditions lead not to digallic acid, but to ellagic acid, which is a stable oxidation product of digallic acid and is frequently formed from the digallic acid nuclei of several tannins, both *in vivo* and *in vitro* (Nierenstein, 1910, 2). It is quite possible that digallic acid is formed and subsequently converted into ellagic acid:



Digallic acid



Ellagic acid

However, if one considers the above-mentioned investigations of Knudson and the pronounced oxidative properties of *Penicillium* (Herzog and Meir, 1908, 1909; Meir, 1909) it is far more likely that the elimination of the glycine radical and the ellagic

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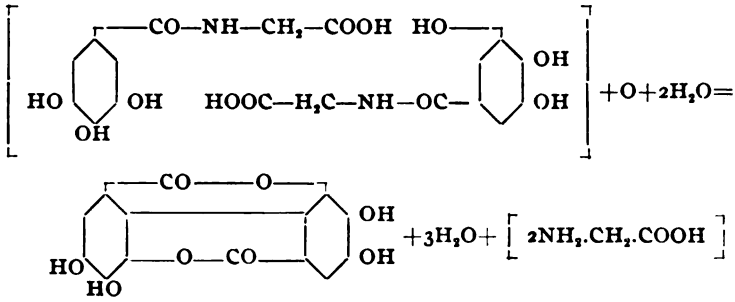
acid formation through oxidation and anhydration (Nierenstein, 1912, 2) take place simultaneously:



This interpretation assumes that the glycine radical is eliminated by hydrolysis, which is hypothetical, as the present investigations have only established the formation of ellagic acid and nothing is at present known as to the fate of the glycine part.

In this connection reference is made to C. L. Berthollet (1809) and also to Merklin and Woehler (1845), who have found ellagic acid in the benzoar-stones of Persian goats, which suggests that galloyl-glycine (trihydroxyhippuric acid) is, perhaps, also formed in the animal organism, especially as ellagic acid has also been found by Woehler (1848) in the bladder of *Castoreum canadense.*

It must, however, be remembered that gallic acid on administration is recovered either as free gallic acid (Stockmann, 1886, 1898; Baumann and Herter, 1877; Harnack, 1898) or in combination with sulphuric acid (Rost, 1898), but never in combination with glycine (Heffter 1905).

Experimental.

Tricarbomethoxygalloyl-glycine.

$(CH_3 — CO_2 — O)_3.C_6H_2.CO.NH.CH_2.COOH.$

Five grams glycine in 75 cc. water and 3.5 grams potassium hydroxide are mechanically shaken for three hours with 26.8 grams tricarbomethoxygalloyl chloride (Emil Fischer, 1908) dissolved in ether, which is added in three portions and cooled before adding. The solution is then left for two or three hours in a cooling mixture and acidified with carefully cooled hydrochloric acid after separation from the ether. The product thus

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obtained crystallizes from alcohol in prismatic needles, which melt at 202°-204° with decomposition and evolution of carbon dioxide. The substance is also soluble in acetone and ethyl acetate. The yield is 94 per cent.

In addition to the usual analysis an hydroxyl estimation by the method of Daniel and Nierenstein (1911) was also made. As in other cases, where the hydroxyls were in the meta-position to the carboxyl groups (Daniel and Nierenstein, 1911; Nierenstein, 1912, 3), nearly 2 per cent. more carbon dioxide was formed than required by theory. This increase is derived from the carboxyl group, which is partly eliminated in these cases by the pyridine (see Bredig and Fajans, 1910; Nierenstein, 1912, 4).

Analysis. 0.2577 g. : 8.3 cc. N_2 at 19° and 767 mm.
0.1850 g. : 0.2816 g. CO_2 ; 0.0565 g. H_2O*
0.2462 g. : 0.0708 g. CO_2 ; (Daniel and Nierenstein)

		Calculated for $C_{15}H_{15}O_{12}N$
N	3.74%	3.49%
C	42.49%	42.76%
H	3.42%	3.69%
CO_2	28.86%	26.92%

* The combustion was carried out in oxygen (see Francis and Nierenstein, 1911.)

Galloyl-glycine.

$(OH)_3C_6H_2.CO.NH.CH_2.COOH.$

Five grams tricarbomethoxygalloyl-glycine suspended in water are treated on the water-bath at about 40° with 50 cc. of a 10 per cent. solution of pyridine and water. The evolution of carbon dioxide is finished in about two hours, when the solid is crystallized from absolute alcohol. It is obtained in cubes, which melt at 282°-283°, the yield being 97-98 per cent. Galloyl-glycine gives like galloyl-leucine (Nierenstein, 1914) only the iron chloride reaction, but not the potassium cyanide reaction for gallic acid (Sidney Young, 1883).

Analysis. 0.2399 g. : 13.3 cc. N_2 at 18° and 755 mm.
0.1758 g. : 0.3057 g. CO_2 ; 0.0572 g. H_2O

		Calculated for $C_9H_9O_6N$
N	6.36%	6.23%
C	47.32%	47.59%
H	3.64%	3.89%

Three grams galloyl-glycine were hydrolyzed with dilute hydrochloric acid (10 per cent.) in a sealed tube and the solution ex-

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tracted with ether. The ethereal part gave on evaporation gallic acid, which had the correct melting point and gave all the specific reactions for gallic acid. The aqueous solution was benzoylated; the hippuric acid obtained melted at 185°-186° and caused no depression when a mixed melting point with hippuric acid was carried out.

Formation of Ellagic Acid From Galloyl-glycine.

Five grams galloyl-glycine and 2 grams sodium bicarbonate are dissolved in 250 cc. of water and the solution saturated with carbon dioxide. The sterilized solution is then inoculated with *Penicillium* (*spec. ?*) grown in a solution of tannic acid, which contains free sugar (see Geake and Nierenstein, 1914). The solution becomes cloudy after standing in an incubator for 32 hours at 42° and in about 78 hours a precipitate begins to be formed. After an incubation of 22 days, the *Penicillium* is carefully removed and the precipitate collected and washed with dilute hydrochloric acid. The product gives the specific Griessmayer reaction for ellagic acid (Nierenstein, 1909) and crystallizes from pyridine in prismatic needles, which contain pyridine (see Perkin and Nierenstein, 1905.) The yields of three preparations were 83, 87 and 84.5 per cent.

For analysis the product was treated with alcohol and dried at 160°.

Analysis. 0.1946 g. : 0.3958 g. CO_2; 0.0395 g. H_2O

	Per cent.	Calculated for $C_{14}H_6O_8$ Per cent.
C	55.50	55.62
H	2.27	1.98

The acetylellagic acid prepared according to Perkin and Nierenstein (1905) crystallized from alcohol in glistening, colorless, flat needles, which commenced to sinter at about 331° and melted at 341°-344°, which agrees with the melting point given by Perkin and Nierenstein.

Analysis. 0.1780 g. : 0.3679 g. CO_2; 0.0489 g. H_2O

	Per cent.	Calculated for $C_{14}H_2O_8(CO\text{-}CH_3)_4$ Per cent.
C	56.37	56.17
H	3.06	2.98

REFERENCES.

Baumann and Herter (1877). *Zeitsch. physiol. Chem.*, 1, 263.
Berthollet (1809). *Mem. phys. et chim. de la Soc. d'Arcueil*, 2, 448.

Digitized by Google

Bredig and Fajans (1910). *Zeitsch. physikal Chem.*, 73, 25.
Connold (1908). British Oak Galls.
(1909), Plant Galls of Great Britain.
Daniel and Nierenstein (1911). *Ber.*, 44, 701.
Fischer (1908). *Ber.*, 41, 2886.
Fischer and Freudenberg (1913). *Ber.*, 46, 1116.
Francis and Nierenstein (1911). *Annalen*, 382, 202.
Geake and Nierenstein (1914). *Ber.*, 47, 891.
Harnack (1898). *Zeitsch. physiol. Chem.*, 24, 115.
Heffter (1905). *Ergeb. Physiol.*, 4, 252.
Herzog and Meier (1908). *Zeitsch. physiol. Chem.*, 58, 35.
(1909). *Zeitsch. physiol. Chem.*, 59, 57.
Knudson (1913). *J. Biol. Chem.*, 14, 159.
Kraemer (1900). *Bot. Gaz.*, 30, 274.
Meier (1909). *Ueber Oxydation durch Schimmelpilze.*
Merklin and Woehler (1845). *Annalen*, 55, 129.
Nierenstein (1909). *Handb. biochem. Arbeitsmeth.* (Abderhalden), 2, 999.
(1910, 1). *Ber.*, 43, 628.
(1910, 2). *Chemie der Gerbstoffe.*
(1912, 1). *Annalen*, 388, 223.
(1912, 2). *Ber.*, 45, 837.
(1912, 3). *Annalen*, 388, 253.
(1912, 4). *Annalen*, 388, 254.
(1914). *Zeitsch. physiol. Chem.*, 92, 53.
Perkin and Nierenstein (1905). *J. Chem. Soc.*, 87, 1415.
Rost (1898). *Ber. Ges. Foerderg. Naturwissenschaft zu Marburg.*, 23, 66.
v. Stockert and Zellner (1914). *Zeitsch. physiol. Chem.*, 90, 497.
Stockmann (1886). *Brit. Med. Journ.*, II. 1077.
(1898). *Archiv exp. Path. Pharmakol.*, 40, 147.
Woehler (1848). *Annalen*, 67, 361.
Young (1883). *Chem. News*, 48, 31.

THE RELATION BETWEEN THE PRICE AND ANALYSIS OF TANNING MATERIALS.*

By John R. Blockey, M.Sc.

Nowadays it is common for tanning materials to be bought on a basis of the tannin content in percentages. Extracts are almost universally bought and sold in this way, whilst raw materials although not bought on a guaranteed strength of tannin, are nevertheless usually valued on this basis. It may be useful, therefore, to inquire into the agreement between the analytical

* *Shoe and Leather Reporter*, Oct. 21 and 28, 1915.

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figures and the results as borne out in practice. Two materials, costing the same amount per unit of tan per ton, by analysis, may give quite different values in practice. This discrepancy is more common in the case of different materials than with the same material, although even in the latter case, the discrepancy may be appreciable. These differences arise mainly from the fact that the analysis is made under conditions quite different from those which obtain in practice. The two chief points of difference are (1) the strength of the liquors, (2) the ratio of the amount of hide substance to tannin matter.

1. Strength of Liquors.

It should be remembered that in analysis according to the official methods of both the I. A. L. T. C. and the A. L. C. A., the solutions should contain approximately 4 grams of tannin per liter, that is, less than ½ per cent. solution. In practice, liquors of such low concentration are only met with in very weak liquors, such as tail liquors or "end suspenders." In sole leather tanning the strength of the liquors may rise to 150° Bark., and over, which will represent a percentage of tannin of anything up to 20. If, for the sake of an average, a liquor of 50° be taken, this will usually contain more than 5 per cent. of tannin, which is more than 10 times as strong as the liquor used for analysis.

(*a*) *Influence on Solubility.*—This difference has an important bearing on the practical interpretation of the analytical figure. At the low concentration of the analysis there will be a great proportion of soluble matter which is not soluble at the relatively high concentration of the tanning liquor. This is merely an example of the usual law of solubilities. Many materials which would show no insoluble matter by analysis, and which would produce at this concentration a clear liquor, would become quite turbid and would contain a considerable quantity of insoluble matter at a concentration such as is common in tannery practice. In this direction, therefore, the tannin analysis errs on the high side and the figure found by analysis is usually higher than is available in practice.

(*b*) *Influence of Temperature.*—The influence of the temperature at which the extract is dissolved is also in the same direction,

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that is to say, that the higher temperature which is used in analysis, will tend to give a higher figure than the temperature used in practice. In the laboratory analysis the extract is dissolved with boiling water whereas in tannery practice, such may be the case in a few instances, but it is much more common, unfortunately, to add the cold extract neat to the cold liquor, thus throwing out of solution a considerable amount of material which would otherwise be rendered soluble and therefore capable of being utilized.

(*c*) *Value of Insoluble Matters.*—Apropos of this subject of insoluble matter, it might be pointed out that recent researches have rather pointed to the fact that the insoluble matters have not such a negative influence as was at one time thought. This, of course, does not apply to the fibrous insoluble matter in raw material such as bark or valonia, but rather to that insoluble matter which has just been described above, that is that matter which will dissolve in hot water or at low concentrations, but which is thrown out of solution on cooling, or at a high concentration. The analytical test for insolubility is an optical one; in the words of the Official Regulations—"the solution must be filtered until it is optically clear, both by transmitted and reflected light." Actually there is no precise line of demarcation between an insoluble and a soluble material, and especially is this the case when dealing with colloidal substances, such as constitute the tanning matters present in tanning materials. As an instance of this might be given the case of quebracho extract. A solution of quebracho extract may be apparently clear by transmitted light, but in order to render it perfectly clear by reflected light a further filtration will be necessary, which would probably cause an increase in the amount of insoluble matter, reckoned on the original extract, of 4 or 5 per cent.. The question is, are these semi-soluble or insoluble products to be reckoned as inert and of no leather-forming value, that is, as valueless as the fibrous matter in bark, or have they any actual tanning value? Recent research points to the latter alternative. Dr. Sommerhoff has shown that it is quite possible to produce leather by the aid merely of materials which are usually reckoned as insoluble. Amongst such materials may be cited freshly deposited sulphur, freshly

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precipitated hydroxides of different metals such as aluminum, freshly precipitated silicates, as well as the insoluble matters present in such extracts as quebracho. By agitation of pelt in aqueous mixtures of these finely divided materials, Sommerhoff found that the latter were absorbed by the pelt and that the pelt assumed leather characteristics.

The writer has seen leather which has been tanned with the insoluble matter of a quebracho extract alone, which was even superior, from the point of view of suppleness, to leather tanned in the soluble matter from the same extract. The bearing of this on the interpretation of a tanning analysis is self-evident. The insoluble matter in a quebracho extract, or in a gambier, is returned by analysis as just as useless as the fibrous matter in such material as mimosa bark, although obviously, according to these later researches of Sommerhoff and others, they have widely different possibilities.

(*d*) *Insoluble Matter in Raw Materials.*—The question of insoluble matter as outlined above, also applies to the case of solid materials, and there is a further point to be noted here, and that is, the difference in fineness of division of the material in analysis and in practice.

In analysis the material is much more finely divided than is ever possible in Works practice; the more finely divided the material the more rapidly will it yield up its soluble matter on extraction with water. The amount of matter which can be extracted by water in analysis but which would not be possible in practice, may be considerable. It is not only due to the fineness of division of the material, but also to the question of color. In order to extract the last ounce of tanning matter from the raw material, the increase in color of the liquor would not be counterbalanced by the increase in the amount of material extracted (this is particularly the case for tanners of leather which is required of a specially light color, such as dressing hides). In any case the analysis is likely to return a certain percentage of matter as being soluble which in practice will almost certainly never be extracted, so that again analysis errs on the high side.

(*e*) *The Deposition of Insoluble Matter.*—Apart from the question of the influence of the strength of the liquor on the

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amount of insoluble matter, which we have seen favors the analytical result, and also apart from the question of the influence of the fineness of division of the material on the amount of the tannin matter extracted, which also favors the analytical result, there is the question of the deposition of insoluble matter from the liquor, even when once the material is dissolved. Even if the tanner succeeds in dissolving as much of the soluble matter as is theoretically possible, that is, as much as is given by analysis, it is not certain that he will be able to utilize it all, because insoluble matter is being gradually formed even when the extract has been dissolved or the material extracted.

A clear liquor made from almost any tanning material will gradually deposit insoluble matter. The nature and amount of this insoluble matter will vary according to the material. In most cases the substances is called "bloom." Valonia and myrobalans are most prolific in the deposition of bloom, but with almost all materials the amount is appreciable. If this insoluble matter is deposited in the leaches or in the liquor it will be just as much lost as if it had never been dissolved. Only if it is deposited on the fibers of the leather can it be of service in the production of leather or can be said to be utilized. The major portion of it is deposited in the liquors on on the surface of the leather to be removed later by scouring. This insoluble matter originates from the soluble tannin matter and is therefore reckoned in analysis as available for the production of leather, so that again analysis tends to give too high a figure for the percentage of tannin.

2. The Ratio of the Amount of Hide Substance to Tannin Matter.

The other main factor which causes a discrepancy between the analytical figure and the practical result is the difference in the proportion of tannin to pelt in analysis and in practice.

In analysis there is always a large excess of hide, so that there is more likelihood of the complete absorption of the tannin matter than in practice where the tannin is always in excess. It would thus seem that again analysis gives too high a figure. This would be true if practical tanning were carried out in such weak liquors as are used in analysis, or if the extent of tanning was only carried as far as with the hide powder in analysis. In practice tanning is carried to a much greater degree than this and enorm-

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ously stronger liquors than this are used. The "leather" produced in analysis from the hide powder, differs considerably from the leather formed in practice. In the former case the "leather" consists of a large excess of hide substance with a small proportion of tannin matter and no free soluble matter, whilst real leather contains hide substance and combined tannin in about equal proportion, together with a large amount of uncombined matter, made up of both tannin and non-tannin matters.

This uncombined matter in the leather is merely the matter which can be dissolved out again by water and the presence of it in leather makes the analytical result rather confusing. This uncombined matter is composed of both tannin and non-tannin matter. The latter constituent is usually considered worthless in that it does not help to produce leather and at any rate the question of the amount of non-tannin matter is only considered in fixing the price of the material.

(*a*) *The Value of the Non-Tannins.*—It may be true that the non-tannin matters do not combine with the hide, but it is not true to say that it is only the matters which are absorbed by hide powder, that is, the tannins, which go to form leather.

Perhaps a concrete example of this would clear the point. The following figures give the analytical results of an average heavily tanned sole leather.

	Per cent.		
A. Moisture	14.0		
B. Hide fiber	31.0	Actual leather substance	
C. Combined tannin	28.3		
D. Matters soluble in water	25.8	Tannins	14.7
		Non-tannins	11.1
E. Mineral ash not included in D.	0.9		
	100.0		

It will be seen that of the matters soluble in water nearly half is composed of what analysis returns as non-tannins. The latter may not combine with the fiber in such a way that it is not capable of being washed out again by water, but it does help to give weight to the leather.

Since the amount of the water-soluble matter in leather depends upon the specific gravity (*i. e.*, Barkometer strength) of the last liquor in which the goods were, and since the specific gravity of the liquor in influenced by the non-tannins as well as of the

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tannins, the amount of the non-tannins in a material should be considered when it is a question of leather sold by weight. It is not implied in this that the quality of a leather is improved by the excess of non-tannins in a material, but merely that the non-tannins may help to give weight to leather and should therefore be taken into account when considering the price of the material.

The value of the non-tannins in the production of leather is a difficult point to settle. Difficulty is met with at the outset in that the definition of non-tannin is not governed by behavior in practice but by analytical conditions. The soluble non-tannins in a material are simply those soluble matter which are not absorbed by hide powder under the conditions of analysis. It has already been shown that these condition differ materially from those which obtain in practice and it is not demonstrably true that the analytical figure is borne out in practice.

(*b*) *Acidity of Liquors.*—The non-tannins may play a much greater part than merely that of giving weight. It is known for instance that the acidity of tannery liquors is influenced by the fermentation of these non-tannins and herein lies aother difference between the conditions of analysis and those of practice.

In practice the liquors are allowed to age, during which time fermentation occurs and acids are produced. In analysis the liquor is detannized immediately, *i. e.*, before fermentation has set in. The effect of the developed acidity on the absorption of tannin by the hide may be considerable, and it is quite possible that what are at present returned as non-tannins may be absorbed by the hide under the conditions obtaining in tannery liquors.

(*c*) *Loss of Tannin by Fermentation.*—The loss of tannin by fermentation in the tannery liquors must, however, be set against the above possibility of the utilization of the non-tannins. It has just been stated that acids are formed in the fermentation of the tan liquors and that these acids may influence the absorption of the soluble matters by the hide. The fermentation takes place in connection with both tannins and non-tannins so that any gain in the absorptive power of the pelt must be counterbalanced by the loss of tannin.

The loss of tannin in this way varies for the different materials; for instance, it is well known that materials which contain

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much sugary matters are prone to fermentation and therefore to loss of tannin *e. g.,* a liquor made from myrobalans ferments much more readily than one made from quebracho.

It is also well known that sumach infusions very quickly lose their available tannin and should therefore only be made up immediately before use.

The question of this loss of tannin by fermentation, etc., should be considered in dealing with the price of a raw material, and it should not be assumed that the amount of tannin given by analysis will all be available in practice.

The Influence of Temperature.

The influence of temperature in the dissolving or extraction of the tanning material has already been discussed and it was pointed out that in analysis boiling water was used whereas in practice water of much lower temperature is often used and that this difference of dissolving temperature tended to make the analytical figure higher than the practical. There is a reverse side to this question. The above point only referred to the temperature at which the material is dissolved or extracted. The temperature at which the liquors are maintained in actual tanning should also be considered. In analysis, the liquors are always cooled down to atmospheric temperature before analysis. In practical tanning this may be the case often but it is not universal.

In extract tanning the liquors are often used hot, whereas sumac and gambier liquors are often used at a temperature considerably higher than atmospheric.

The effect of this difference of temperature between analysis and practice may have appreciable influence on the amount of insoluble matter. For instance, a gambier containing 5 per cent. of insoluble matter at the temperature of analysis may only show 2 per cent. at the temperature at which it is used, so that analysis in this case gives too low a figure.

The Effect of Mixtures of Tanning Materials.

In analysis, materials are analyzed separately whereas in practice materials are almost invariably blended. The influence of the blending of materials on the amount of available tannin matter may be considerable. The effect of blending two materials might be to cause matters, which analyzed separately, would be

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called non-tannins, to be absorbed by pelt and thus to become tannins. The reverse also might occur. A more probable effect would be on the conversion of insoluble matters into soluble ones, or the reverse. It is, for instance, known that by blending some of the new synthetic tanning materials (Neradol) with quebracho, a proportion of the insoluble matter in the latter is rendered soluble and absorbable by hide.

From the above considerations it will be seen that the agreement between practical behavior and the analytical result is by no means simple or close.

When basing the price of a material on the analytical figures it is necessary to take into account many factors, such as (1) the strength of the liquors to be used, (2) the temperature, (3) the length of time the liquors are allowed to stand, (4) the effect of mixing the material with others, (5) the acidity of the liquors, etc.

Summing up, it might be said that analysis usually gives a higher figure for the amount of tannin matter than is available in practice, although under certain circumstances the reverse may hold. Generally, the analytical figure might be taken as representing the maximum amount of material which could be utilized under ideal conditions.

THE TANNIN CONTENT OF PACIFIC COAST CONIFERS.*

By H. K. Benson and Thos. G. Thompson.

The tannin extract industry of the United States utilizes for its raw material chestnut wood and the bark of the Eastern hemlock and the chestnut oak. From these species a standard extract containing 25 per cent. tannin is manufactured, annually amounting to over 200,000,000 pounds. An equal or greater quantity of extract is either imported, or made from materials imported, of which quebracho is of chief importance. In view of the large sources of available supply of tannin-containing materials on the Pacific Coast, a study was made of the tannin content of Western hemlock, Douglas fir and Western spruce.

* *J. Ind. and Eng. Chem.*, Nov. 1915, pp. 915–16.

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Western Hemlock.

The Western hemlock extends from Alaska to Marin County, California, and eastward, in some places, as far as Montana, thriving in the cool, moist climate characteristic of western Washington and Oregon. It grows along with spruce, cedar and fir, often being left as useless by the timber cutters. An excellent example of the distribution of these trees is found in a recent survey of the merchantable timber of the Olympic National Forest. It was found that out of this forest, containing 25,500,000,000 feet of timber, 35 per cent. was Western hemlock, 37 per cent. Douglas fir, and the remainder spruce and cedar.

The bark of the Western hemlock is thinner than that of the Eastern hemlock, but, as is commonly known, it contains a higher tannin content. This fact was first brought to the attention of the Washington public in 1893 when several samples of the bark were submitted to Dr. H. W. Wiley, who reported the following analyses:

Sample	Ashford	Enumclaw
Moisture	10 55	10.01
Total solids	24.03	22.16
Soluble solids	22.59	20.58
Reds	1.44	1.58
Non-tannins	6.59	5.76
Available tannins	16.00	14.86
Woody fiber	65 42	67.83

The first results that were published[1] calling attention to the differences in percentage of the tannin content of the Western and Eastern hemlock were the following analyses made by H. G. Tabor of hemlock bark from trees in Washington, Pennsylvania and Quebec:

Source	Washington	Pennsylvania	Quebec
Tannin	17.04	13.28	10.16
Non-tannin	6.40	7.52	4.56
Reds	1.56	3.48	1.92
Woody fiber	75.00	75.72	83.36

Western hemlock bark has been used as the exclusive tanning agent in at least one tannery in Washington for a number of years. This concern manufactures chiefly skirting leather for saddles. Its larger use has been prevented by the lack of tan-

[1] *Hide and Leather*, June 24, 1893.

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neries, due to economic reasons, rather than unsuitableness. The prevailing cost of hemlock bark f. o. b. tannery has been $11.50 per cord.

Experimental.

Inasmuch as few references to the tannin content of Douglas fir and Western spruce could be found, and as far as is known

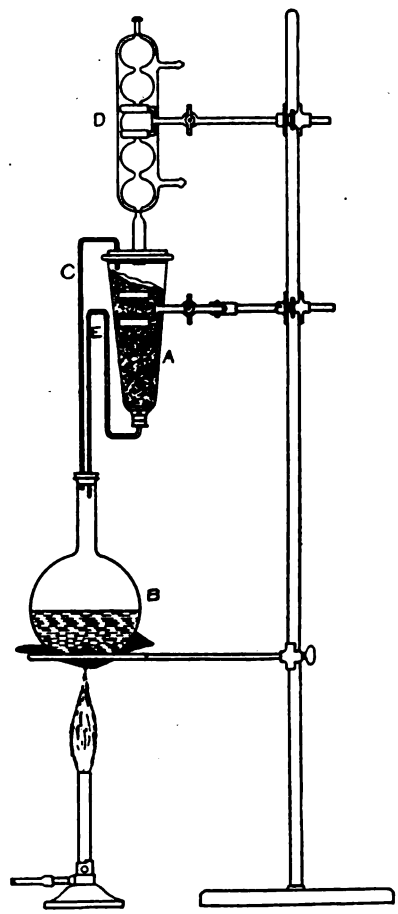

Fig. I

no effort has ever been made to demonstrate the tannin content of sawmill waste from these species, an experimental study was undertaken.

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Preparation of Sample.—The sawmill waste taken for analysis consisted of bark, slabs, and sawdust from the cross-cut saws. Samples of 100 pounds were taken for the bark, from 100 to 150 pounds for slabs, and about 25 pounds for the sawdust. The bark and the slabs were each reduced in a Mitts and Merrill chipper and the chips quartered to obtain an average sample. Before subjecting the sample to analysis it was further reduced to a fine powder in a Grumbaugh mill.

Extraction of Sample.—The apparatus used for extraction is shown in Fig. 1. From 50 to 75 grams of the sample were placed in the percolator *A*. The flask *B* contains the water for extraction. On boiling, the steam flowed through the tube *C*, and entered the percolator where partial condensation occurred in *D*. Boiling water continually drops upon the material in *A* until it reaches the height indicated by *E*, after which it is returned to the boiling vessel *B*. To prevent rifts or channels in the sample, the latter was mixed with broken glass before extraction, and to prevent particles of bark or wood from siphoning over with the liquid, a small perforated porcelain disk and glass wool were placed over the outlet tube. It was found advisable to use as large an outlet tube for the condenser as possible and to spread glass wool or wire gauze over the top of the sample in the percolator. Both the extraction and the analysis were made in accordance with the official method of the American Leather Chemists' Association.

Tannin Content of Douglas Fir.

The extract obtained from the Douglas fir was reddish brown in all cases except from the freshly cut bark which was yellow-brown and contained a yellow precipitate. The logs from which the samples were obtained had been cut for a period of eight months and during a portion of this time they were in water. However, the bark of the Douglas fir is so thick that there is probably very little loss of tannin by leaching in floating the logs to the sawmills. From the yields given in Table I, it is shown that the cambium layer, which is dark brown in seasoned wood and yellow-brown in freshly cut wood, contains most of the tannin. When a sample of bark is taken from a seasoned log not all of the cambium layer is taken. The slab, however, contains

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the cambium layer in its entirety with a relatively small quantity of wood in addition to the bark proper. The analyses of various samples appear in Table I, the results being reported on the dry material.

TABLE I.—TANNIN CONTENT OF DOUGLAS FIR.

Sample	Sawmill bark	Sawmill slab	Fresh bark	Cambium layer	Sawdust
Total solids	14.75	14.92	11.31	21.96	5.78
Soluble solids	13.36	13.02	9.36	19.28	4.40
Reds	1.39	1.90	1.95	2.68	1.38
Non-tannins	7.02	7.10	6.74	9.36	3.34
Tannin	6.34	5.92	2.62	9.92	1.06
Moisture	9.06	6.91	14.27	20.59	15.51

TANNIN CONTENT OF WESTERN SPRUCE.

The extract from spruce was a clear brown in color. The bark is much thinner than in fir. On account of remoteness of the mill from which the samples were obtained no history of the logs is available, but it is probable that they were floated in water a longer period than in the case of the fir logs. While check analyses were made, time did not permit as complete an examination as for fir. The results of the analysis, reported on a dry basis, are given in Table II.

TABLE II.—TANNIN CONTENT OF WESTERN SPRUCE.

Sample	Sawmill bark	Sawmill slab
Total solids	12.83	11.25
Soluble solids	12.30	10.38
Reds	0.53	0.87
Non-tannins	6.42	6.79
Tannin	5.88	3.69
Moisture	15.23	9.15

TANNING VALUE OF FIR EXTRACT.

The fir chips from the bark and slabs not required for samples were extracted by the West Coast Tanning Company, Seattle, and several skins tanned in the resulting extract. A very desirable leather was produced, having a color similar to that obtained from oak tannin.

COMMERCIAL POSSIBILITIES FOR FIR EXTRACT.

When it is remembered that the tannin content of chestnut wood is 6.62 per cent., it appears that the low cost of fir slabs containing an average of 5 per cent. tannin should make the use of

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fir slabs a possible raw material for the tannin extract industry. It is known to the writers that fir slabs can be purchased from some of the mills at as low a cost as 75 cents per cord. In mills located in large cities, where they are sold for fuel, the cost is usually $1.50 to $2.00 per cord. Compared with Western hemlock bark at $11.50 per cord, it is found that three cords of fir slabs will yield as much as one cord of hemlock bark but at less than one-half the cost of the bark.

Conclusions.

1. The tannin content of fir sawmill waste is above 5 per cent. while that of spruce is above 4 per cent.

2. It is believed that fir waste is a suitable material for use in the tannin extract industry.

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EXPOSITION OF CHEMICAL INDUSTRIES.

At the Chemists' Club, 52 East 41st Street, New York, Wednesday evening, November 10th, was a notable gathering of the following well known industrial chemists, at a dinner tendered by the management of the exposition, to discuss plans for the next National Exposition of Chemical Industries: Raymond F. Bacon, Chas. H. Herty, Henry B. Faber, A. D. Little, E. F. Roeber, George D. Rosengarten, T. B. Wagner, L. H. Baekeland, M. C. Whitaker, B. C. Hesse, Adriaan Nagelvoort and Chas. F. Roth; also Mr. R. G. Hollaman and Mr. F. W. Payne of the International Exposition Company were present, all of whom will serve on the Advisory Committee for the 1916 National Exposition of Chemical Industries to be held at the Grand Central Palace, New York City, week of September 25, 1916. At this meeting Dr. Chas. H. Herty was elected to serve as chairman of this committee for the coming year.

Plans for enlarging and increasing the scope of the coming Exposition were laid, which will assure a very large exposition both from the attendance standpoint as well as exhibits. The plans include using several floors of the Grand Central Palace, with speakers in the evening and motion pictures during the day

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from 11 A. M. to 7 P. M. Next year an entirely new set of motion pictures will be shown, covering a very much wider field of industrial activities.

ABSTRACTS.

Tanning Materials in Brazil. *Commerce Reports.*—The tanning materials used by Brazilian tanneries include: Carbatimao bark, obtained from the State of Minas Geraes, considered to be an excellent tanning material, containing about 60 per cent. of tannin; angico bark, also obtained from the State of Minas Geraes, regarded as a good tanning material, very light in color, but containing only about 28 per cent. of tannin; and mangue bark, which is found all along the Brazilian coast and is well known in the United States and Europe under the names of mangrove, palétuvier, etc. There are no factories in this country manufacturing tanning extract, the bark being employed as such. It is said that the principal reason for the undeveloped condition of the tanning industry in Brazil—which annually exports raw hides to the value of many millions of dollars and imports large quantities of foreign-tanned leather for manufacturing purposes—may be principally attributed to the scarcity of tanning material. There is only one important tannery in Rio de Janeiro, Sao Paulo and Porto Alegre each have several small ones. The manager of the Rio firm states that although its establishment is working day and night, owing to the increased demand for leather in Europe, with a daily production of about 200 hides, it is believed that before many more months the factory will either have to close down entirely or work shorter hours, owing to the apparent growing scarcity of tanning materials. Brazil, for the present at least, is not in position to export tanning materials. The difficulty which this country has found in the exploitation of its valuable hardwood forests (the best varieties of trees being situated far from railway facilities) and the high cost of labor and transportation at most interior points seem to have hampered the extraction of tanning materials, of which the country should possess large quantities. At present rates of exchange the price of carbatimao and angico bark in Rio de Janeiro and Sao Paulo averages about $30 United States gold per metric ton (2,204.6 pounds). Barks for tanning may be exported from the Pernambuco district to the United States. Those most used are the angico and mangue, the former being the more abundant. Mangue leaves are also used, but they are not available for exportation because they easily lose their properties.

Guara. F. ASHWORTH. *London Shoe Trade Journal*, through *S. & L. Rep.*, Nov. 11, 1915. Microscopic examination confirms Eitner's statement that guara is the ground-up fruit of a species of divi. Practically all the tests for pyrogallol tannin are met. Bromine water gives no

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precipitate, iron alum, violet-blue coloration, very slight precipitate with formaldehyde and hydrochloric acid, pink to purple coloration with Bennett's iodine test. The sulphuric acid test, however, is similar in result to catechol tans, crimson pink changing to pink on dilution. Guara does not give the excessive fermentation so characteristic of divi. It is excellent for developing acidity in tan-liquors, and has a good influence on the color of the product when used with untreated quebracho. It does not draw the grain, but gives a soft and mellow tannage. Four analyses are given, tannin ranging from 43.5 per cent. to 48.8 per cent., non-tans from 23.1 per cent. to 23.8 per cent. and moisture from 9 per cent. to 10.7 per cent. Skins tanned entirely with guara resembled gambier tannage, rather than sumac or molybalan. The well-nourished appearance of the leather may be due to the character of the non-tans.

The Oxidation of Sewage without the Aid of Filters. E. ARDERN and W. T. LOCKETT. *J. S. C. I.*, Sept. 30, 1915. An abstract of a previous article on the same topic by the same authors appeared in this JOURNAL last year, page 331. The agent of purification employed is "activated" sludge. This was produced in the original experiments by aerating a quantity of sludge continuously until it was completely nutrified, then allowing it to settle, adding to the sludge a further quantity of sewage, again aerating until nitrification was complete, settling drawing off the clear liquid, adding to the sludge more sewage, and so on. The time required for complete nitrification in the first place was about 5 weeks, but after many repetitions, the period was reduced to 24 hours or less. The present paper deals with (1) methods of producing activated sludge, (2) the volume of air necessary for the successful working of the method, and (3) the most advantageous proportion of activated sludge to employ. The following method for producing activated sludge was found practicable: A mass of sewage contained in a suitable tank is aerated for 9 hours or more, then allowed to settle, the partly clear liquid drawn off and a fresh quantity of sewage added. This process is repeated many times, so as to accumulate a large quantity of partially activated sludge, which is then continuously aerated until nitrification is complete. This last process requires about 15 days, some carbonate of soda being added from time to time. The activated sludge so obtained, on being agitated in contact with raw sewage by the passage of air produced complete nitrification of the new charge in 26 hours, and after 25 repetitions the nitrification of a fresh batch was complete in 8 hours. This period was finally further reduced to 6 hours. Experiments were tried to determine whether the use of hydroxides of iron, aluminum or manganese had any beneficial effect in connection with the use of activated sludge. All these experiments had negative results. Extended experiments on the required quantity of air indicate that 6 cubic feet of air per hour per square foot of tank area is sufficient for the complete nitrification of ordinary sewage. More rapid nitration can be secured by using a larger proportion of activated sludge to sewage than the standard

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amount employed in most of the experiments, which was 1 of sludge to 4 of sewage, the volume of the sludge being measured after 2 hours' settlement, but the increased capacity of tanks necessary to deal with a given quantity of sewage introduces a practical problem of some complexity when the best proportions for an actual installation are sought. The cost of the process has been approximately worked out, and lies between $2.50 and $5.00 per million gallons.

CORRECTIONS.

July number, page 380, line 7; for "pages 374 and 375" read "pages 378 and 379."

September number, page 456, line 1; for "in well known" read "is well known."

Page 456, line 2; for "quantities of saponifiable are liable" read "quantities of unsaponifiable are liable."

November number, page 561, 7th line from bottom; for $C_{18}H_{33}O_2.O.SO_3H$ read $C_{18}H_{33}O_2.O.SO_3H$.

PATENTS.

Tanning Agents. British Patent 3382. (Grant of patent suspended.) J. Y. JOHNSON, London, assignor to the Badische Company.

Formaldehyde Derivatives. Compounds having tanning properties are obtained by treating, under pressure and at a temperature above 100° C., hydroxy compounds of the benzene or naphthalene series, or salts thereof, with formaldehyde, or a body yielding formaldehyde, and a neutral or acid sulphide; the reaction mass is preferably kept alkaline throughout the process. According to examples, products are obtained from the following parent materials: phenol, formaldehyde, and sodium sulphite; sodium phenolate and sodium formaldehyde bisulphite; *m*-oxybenzoic acid, formaldehyde, and sodium bisulphite, cresol monosulphonic acid, formaldehyde, and sodium bisulphite.

Leather Rolling Machine. British Patent 15,646. C. VOSS, Newark, N. J.

Positively Driven Ring Roll. U. S. Patent 1,158,627. W. E. BROUGHTON, Peabody, Mass., assignor to the Turner Company.

Apparatus for Dissolving and Treating Tanning Extracts. U. S. Patent 1,158,304. EMIL SCHAUB, Weehawken, N. J., assignor to Paul Voiges, N. Y.

Rotating Tool Machine. British Patent 14,031. L. P. MORIN, Lagny, France.

Tanning and Waterproofing Leather. U. S. Patent, 1,157,952 J. MOSZYNSKI, Phila.

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